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Modelling of Contaminant Migration in Acidic Groundwater Plumes at Uranium Tailings Impoundments: Adneut3

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MODELLING OF CONTAMINANT MIGRATION IN ACIDIC GROUNDWATER PLUMES AT URANIUM TAILINGS IMPOUNDMENTS: ADNEUT3

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SUMMARY

This report describes the creation and application of ADNEUT3, the latest addition to the ADNEUT (Acid-Drainage NEUTralization) family of computer programs for simulating acid-drainage transport and neutralization. The creation of ADNEUT3 involved the expansion of ADNEUT1 to allow variable input conditions such as changing input solution with time, variable initial amounts of minerals through the simulated streamtube, variable velocity through the streamtube, and variable solubilities for relevant minerals dependent on aqueous chemical composition.

Concepts for simulating acid-drainage neutralization are reviewed and ADNEUT3 is then applied to a field-study site of acidic contaminant migration from the Nordic Main uranium-tailings impoundment near Elliot Lake, Ontario. A sensitivity study is first implemented to calibrate ADNEUT3 to the results of the 1979 to 1983 field studies. Then ADNEUT3 is used to define probable past conditions at the site which are not reliably known. In particular, ADNEUT3 is used to help identify 1) the approximate year when acidic seepage began leaving the tailings impoundment (1966-1967), 2) the past chemical composition of the seepage (somewhat more acidic for a short period of time), and 3) the location of the source area within the tailings for the acidic seepage (near the impoundment dam, close to the field site).

Finally, ADNEUT3 is used to predict future contaminant migration. Results indicate that hundreds of years are required under present conditions for the most acidic water with associated high levels of contaminants to migrate about 100m from the tailings impoundment. The cause of this slow movement is the significant neutralization capacity of the aquifer. If acid production within the tailings decreases in the future, migration rates of contaminants will also decrease.

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1. INTRODUCTION

ADNEUT3 is the latest addition to the ADNEUT (Acid-Drainage NEUTralization) family of computer programs which simulate acid-drainage groundwater transport and neutralization through a streamtube divided into a series of cells. ADNEUT1 and ADNEUT2, which are described in detail in Morin (1983) and Morin and Cherry (in prep, A), are limited by the requirement of identical initial conditions for all cells. ADNEUT3, which is an expanded and more flexible version of ADNEUT1, has been developed to accomodate unique conditions for each cell; this allows the simulation of such events as variable velocity and variable solubilities for a mineral through the simulated streamtube.

ADNEUT4 is currently under development for inclusion in Dubrovsky (in prep). ADNEUT4 will be an expanded version of ADNEUT3 and will contain at least one Al-OH-SO_4 mineral.

2. REVIEW OF ACID-DRAINAGE NEUTRALIZATION AND THE SUB-REGION CONCEPT

Upon evaluating one detailed field study in Elliot Lake and reports of six other studies, Morin (1983) divided subsurface seepage from acidic uranium-tailings impoundments into three zones. The first zone is the "inner core", which is adjacent to the impoundment and contains unaltered or slightly altered acidic water seeping from the tailings. The inner core contains water with relatively high concentrations of iron and sulfate. Far from the impoundment lies

the "outer zone", which contains neutral-pH water with relatively low concentrations of iron and sulfate. The "neutralization zone" is the transition region between the inner core and outer zone.

As inner-core water enters the neutralization zone, pH is neutralized by dissolution of carbonate minerals, aqueous iron is removed by replacement of calcite by siderite and/or by precipitation of $Fe(OH)_3$, aqueous aluminum is removed by the precipitation of Al-OH minerals, and aqueous sulfate is removed by the precipitation of gypsum. After the groundwater completely passes through the neutralization zone and these reactions are complete, the chemical composition of the water is that of the outer zone. In this way, inner-core water is constantly "laundered" by the neutralization zone, preventing the rapid migration of inner-core conditions; however, because mineral consumption and formation occurs in the neutralization zone, the neutralization zone slowly migrates away from the tailings impoundment. Field studies indicate that the migration of the neutralization zone and the inner core is significantly retarded with respect to groundwater velocity. Consequently, the accurate prediction of contaminant migration from acidic uranium-tailings impoundments requires the detailed simulation of neutralization-zone reactions.

ADNEUT results have shown that the neutralization zone is not a single entity, but in fact consists of several dis-

tinct "sub-regions". The aqueous chemistry of each sub-region is dominated by one of the precipitating-dissolving minerals mentioned above, and the simulation results are quite sensitive to the characteristics and number of sub-regions.

There are four possible sub-regions and each is named after the dominating mineral: calcite sub-region, siderite sub-region, $Al(OH)_3$ sub-region, and $Fe(OH)_3$ sub-region (gypsum does not usually form an independent sub-region). Each dominating mineral is associated with an "equilibrium pH". If solution pH is below a mineral's equilibrium pH, the mineral dissolves, thereby raising solution pH to the equilibrium pH. If solution pH is above a mineral's equilibrium pH, the mineral precipitates. In reality, a mineral's equilibrium pH is a function of the solubility of the mineral, the number of other minerals present, the solubilities of the other minerals, and the solution composition; this complexity will be addressed in a following section.

One set of hypothetical equilibrium pH's (Morin, 1983) is: calcite = 5.7, siderite = 5.2, $Al(OH)_3$ = 5.1, and $Fe(OH)_3$= 3.5. Using these equilibrium pH's, a detailed scenario for contaminant migration can now be formulated. When inner-core water seeping from the tailings first enters the subsurface, it encounters calcite. Calcite then dissolves, solution pH increases to 5.7, and siderite, $Al(OH)_3$, and $Fe(OH)_3$ precipitate. After all calcite adjacent to the

impoundment is consumed, siderite dissolution begins and raises solution pH to 5.2, and $Al(OH)_3$ and $Fe(OH)_3$ continue to precipitate, while calcite farther from the impoundment begins to dissolve. After all siderite adjacent to the impoundment is consumed, $Al(OH)_3$ dissolution begins and raises solution pH to 5.1, while siderite begins dissolving farther from the impoundment after the farther calcite is dissolved, etc. In this way, a series of sub-regions exists along a flowpath with pH being incremented from the inner core to the outer zone (Figure 1). ADNEUT results show that each upgradient sub-region migrates at a slower rate than downgradient sub-regions, resulting in profiles as shown in Figure 1 for pH and several aqueous constituents. Morin (1983) found that all sub-regions need not be present at a site and that equilibrium pH's are site-dependent.

3. THE COMPUTER MODEL, ADNEUT3

3.1 DETAILS OF ADNEUT3

ADNEUT is a family of one-dimensional cell models which simulate acid-drainage transport and neutralization through an isolated groundwater streamtube that is divided into a series of cells. To lower costs, ADNEUT1 was designed so that all cells had identical conditions (size, velocity, amount of minerals initially present, etc.). Although ADNEUT1 provided satisfactory simulations, the capability of

variable input conditions was expected to provide better simulations (Morin, 1983).

ADNEUT3 allows variable input for a simulation. In particular, ADNEUT3 allows 1) the input solution to the streamtube to change with time, 2) each cell to have unique initial amounts of minerals, 3) the simulation of variable velocity through the streamtube, and 4) a unique solubility for each mineral in each sub-region. The first variable input, changing input solution with time, is valuable for long-term simulations during which the rate of acid production changes. The second variable input is not a major benefit in this study because of the lack of detailed spatial data; however, this capability may be of importance in simulating migration in the tailings. The third variable input is of value in simuations covering long distances over which groundwater velocity varies significantly. The fourth variable input is extremely important in correctly simulating retardation factors and aqueous chemistries of the sub-regions.

The first variable capability of changing input solution with time is implemented by allowing the user to enter each solution and the time after which each solution flows into the streamtube. ADNEUT3 reads and speciates all input solutions before a simulation begins so that 1) any errors in the solutions will be detected before a great deal of CPU time is used and 2) a unit channel or device will not be

kept open for transmitting data for a significant length of real time. The disadvantage of this approach is the increased memory storage requirement for retaining all input solutions.

The second variable input of unique amounts of minerals in each cell is implemented simply by allowing the user to enter the amounts of each mineral in weight-percent for each cell.

The third capability of variable velocity through the streamtube is more difficult to implement than the other variable inputs. There are two basic methods for simulating variable velocity in a one-dimensional cell model: using a series of cells of identical dimensions with a different residence time, i.e. length of time during which a mass of water resides in a cell, for each cell or using a series of cells of varying dimensions with identical residence times for all cells. The first alternative may easily lead to mass-balance errors and, thus, is not used in ADNEUT3.

Original plans for ADNEUT3 called for the internal calculation of cell size from the user-supplied velocity distribution; however, this was rejected because the cell sizes and, thus, cell locations would not be known before the simulation began. By not knowing cell sizes and locations, the user could not define the desired amount of minerals for each cell if the amounts varied spatially and the user would not know the total number of cells which directly affects the cost of the simulation.

Therefore, ADNEUT3 requires the user to input the total number of cells, the residence time, and the length and groundwater velocity for each cell. Because the residence time is set, when the groundwater velocity for a region to be represented by a cell is known, the length of the cell can be calculated from:

LENGTH = RES TIME * VELOCITY

For example, if the calculated LENGTH covers only half the region represented by VELOCITY, the user may add another cell of identical length or increase RES TIME by a factor of 2. ADNEUT3 implicitly adjusts the height and width of each cell so that the volumes of all cells are identical and mass balance is maintained. ADNEUT3 rechecks the residence time for each cell by the equation, CELL LENGTH/CELL VELOCITY, and stops execution if a cell's calculated residence time differs significantly from the designated overall RES TIME.

The fourth variable input of a unique solubility for each mineral in each sub-region is implemented simply by the input of log[solubility product at solution temperature] of each mineral in each sub-region. By entering 0.0 for any log value, ADNEUT3 will use its internal solubility product for the mineral.

ADNEUT3 identifies the sub-region in which each cell lies by first reaching equilibrium with the solid and liquid phases and then checking if the mineral that has been pro-

ducing its equilibrium pH in the cell is still present. If the mineral is still present, results are stored and the simulation continues. If the mineral has been totally dissolved, then the cell now lies in a new sub-region, and ADNEUT3 now implements the correct solubility products for the new sub-region and re-calculates equilibrium with solid and liquid phases.

Although ADNEUT3 accepts any value for the solubility products, the user of ADNEUT3 must be careful in the choice of the values. If greatly different solubilities are used in adjacent sub-regions for a mineral, an oscillation of sub-regions may result. For example, the solubility of calcite in a particular simulation is high in the calcite sub-region and very low in the siderite sub-region. As all calcite in a cell dissolves, the cell enters the siderite sub-region. If the solubility of calcite in the siderite sub-region is low enough, calcite precipitates as siderite dissolves. ADNEUT3 detects the calcite, places the cell back into the calcite sub-region, the calcite begins to dissolve, and the oscillation continues. ADNEUT3 detects such oscillations, issues an error message, and halts execution. It is emphasized here that sub-region oscillations are user errors caused by greatly variable solubilities for a mineral.

The ADNEUT family of programs can be used in three modes. The first and most expensive is the multi-cell mode in which

several cells are used in the simulation (Figure 1). The multi-cell mode provides equilibrium pH's, aqueous concentrations, spatial data (length), and temporal data (migration rate) for all sub-regions. The second and less expensive mode is the two-cell mode which provides equilibrium pH's, aqueous concentrations, and retardation factors for all sub-regions; the lengths of sub-regions at a particular time must be calculated by hand with some difficulty. The least expensive mode is the one-cell mode which provides only equilibrium pH's and aqueous concentrations for the sub-regions; because inner-core water is the input solution for all sub-regions in this mode, reliable data on retardation factors cannot be obtained. Detailed information on the comparison and implementation of these modes can be found in Morin (1983) and Morin and Cherry (in prep, A). ADNEUT3 can be used in these modes, although many of the benefits of ADNEUT3 apply only to the multi-cell mode.

Changes have been made in ADNEUT3 during this study to improve efficiency and accuracy as much as possible. Where these changes were of value to ADNEUT1 and ADNEUT2, these programs were also adjusted. A listing of ADNEUT3, instructions for input, sample input, sample output, definition of variables, and a flowchart for the ADNEUT programs can be found in Appendix A.

3.2 DETAILS OF SIMULATING MIGRATION OF THE NEUTRALIZATION ZONE BY A CELL MODEL

This section addresses the relationships between cell length, residence time, time steps, and accuracy of results in cell models such as ADNEUT3.

Figure 2 contains the results of two hypothetical simulations with identical input conditions except for cell length and residence time (cell length = residence time x groundwater velocity in cell). The hypothetical retardation factors for each sub-region are also indicated in the figure.

Simulation B in Figure 2 involves cell lengths and residence time that are a factor of 5 greater than for Simulation A. As a result, when a sub-region moves into a cell in Simulation B, there is an instantaneous movement of 5x the distance that occurs when a sub-region moves in Simulation A. However, because there are 5 time steps (length of time step = residence time) in Simulation A for every time step in Simulation B, both Simulations should show identical results after equal amounts of simulated time. As seen in Figure 2, identical results are not obtained after equal amounts of time, e.g. 25 time steps for Simulation A and 5 time steps for Simulation B. The cause of this disagreement is that the lengths, i.e. number of cells in length, of each sub-region in Simulation A are not all 5 cells or a multiple of 5 cells; as a result, Simulation B, which approximates 5 cells in Simulation A by 1 cell, cannot reliably represent the trend. Of course, as simulated time increases and the

length of sub-regions increase, Simulation B will better approximate Simulation A, although some detail will still be lacking.

By extrapolating the above discussion to smaller cell lengths, it becomes obvious that, if each cell in Simulation A were divided into 5 cells, then Simulation A only approximates early movement over its first 5 time steps as Simulation B did over its first 5 time steps. Thus, to satisfactorily represent very early times, cell length must approach zero, thereby ending discretization and truly representing reality. The user of a cell model like ADNEUT3 should remember the inaccuracy at early times and the increase in accuracy as time increases.

The points addressed so far in this section can also be approached from a different point-of-view, which illuminates other features of cell-model simulations. Comparison of cell patterns, i.e. number and locations of cells occupied by a "C", an "S", etc., in Figure 2 indicates that all simulations will show identical cell patterns after equal numbers of time steps. (Note arrows connecting identical patterns after an equal number of elapsed time steps in Figure 2.) Because execution costs are related to the number of time steps, Simulation B has simulated at equal cost sub-region migration for 5x as many years as Simulation A after an identical number of time steps or, in other words, Simulation B simulates a certain amount of time for 1/5 the cost

of Simulation A. The inaccuracy of spatial data as discussed in previous paragraphs is the disadvantage of this cheaper simulation.

The above relationship of cell patterns can be employed by users who desire more detail at early times. For example, if cells and residence time for Simulation A were divided by 5, then the early migration currently represented by time steps 0 to 5 in Simulation A would be more accurately represented by the migration pattern represented by time steps 0 to 25 in Simulation A, keeping in mind that 5 cells in time steps 0 to 25 now represent 1 actual cell in time steps 0 to 5 in Simulation A of Figure 2. In this way, more detail on early times can be obtained from existing information.

In summary, there are important relationships between cell length, residence time, time steps, and accuracy of results. The user should be aware of these relationships and the user must determine appropriate cell length and residence time so that 1) sufficient detail is obtained, 2) the number of time steps is kept to a minimum, and 3) enough time steps are used so that the inaccuracy at early times is not a problem. Simulation results can be extrapolated to very early times if such information is required.

In relation to ADNEUT, two additional comments must be made. First, the discussion in this section pertains only to the multi-cell mode; the two-cell mode by which only re-

tardation factors are obtained is not affected by the relationships. Second, because ADNEUT3 simulates variable velocity in the streamtube by adjusting lengths of each cell, variations in velocity by one order of magnitude, for example, require cells that vary in length by one order of magnitude. If a reasonable length is chosen for the largest cell, the smaller cells will be too small and numerous (too expensive). If a reasonable length is chosen for the smallest cell, the larger cells will be too long, not providing sufficient detail. The user must make a compromise between these extremes.

3.3 EXECUTION TIMES AND COSTS FOR ADNEUT3

This section briefly presents execution times in CPU seconds per cell per time step (seconds/CTS) and execution costs per cell per time step ($X/CTS) for ADNEUT3 on an IBM4341 computer with a Fortran VS compiler. It is emphasized that execution times and costs per cell per time step are highly dependent on the compiler, the computer, the computer rates if a time-sharing system, the total number of time steps, the input solution, the number of sub-regions, and the number of cells. Times and costs per cell per time step have been observed to vary well over 2 orders of magnitude with only a change in input solution. As a result, the following values are for general evaluation only.

Over tens of time steps in the two-cell mode, results are 7-21 CPU seconds/CTS ($0.95-$3.00/CTS). Over thousands of time steps:

no. of cells	time in seconds/CTS	costs in $/CTS
6	0.22	$0.03
12	0.148-0.097	0.02-0.013
14	0.12	0.017
27	1.68 (perturbations)	0.22
27	0.0063 (very dilute solution)	0.00085

4. APPLICATION RESULTS OF ADNEUT3

4.1 SEEPAGE AREA A, NORDIC MAIN IMPOUNDMENT, ELLIOT LAKE, ONTARIO

The Nordic Main uranium-tailings impoundment (Figure 3) near Elliot Lake, Ontario, is the site of a continuing field study of acidic seepage migration. The area containing the major contaminant plume is designated "Seepage Area A". Latest results of the Area A study can be found in Morin et al. (1982), Morin (1983), Morin et al. (in prep), Morin and Cherry (in prep, B), and Morin and Cherry (in prep, C). Diagrams of aqueous chemical trends along the 2-D vertical centerplane of the contaminant plume and along the 1-D centerline are presented in Figures 4 to 8. ADNEUT3 has been applied only to this site in this study.

With an initial solid-phase content of 0.85 wt-% calcite, ADNEUT results indicate the presence of three sub-regions in Area A: calcite (equilibrium pH = 5.7), siderite (equilibri-

um pH = 5.3), and $Al(OH)_3$ (equilibrium pH = 5.0). The calcite sub-region is synonymous with the outer zone near the impoundment dam. Additional data, including retardation factors for each sub-region with respect to groundwater velocity, are tabulated in Table 3. (The migration rate or retardation factor of a sub-region is defined as the migration rate or retardation factor of the contact with the adjacent upgradient sub-region; e.g. the migration rate of the calcite sub-region is the migration rate of the contact of the siderite and calcite sub-regions.)

4.2 SENSITIVITY OF ADNEUT3 RESULTS TO SOLUBILITY VALUES IN SEEPAGE AREA A

For the purpose of this section on sensitivity tests, ADNEUT3 was used in the two-cell mode.

Morin (1983) made an informal sensitivity study on the input parameters to ADNEUT; a formal sensitivity study was not warranted because sensitivity of results is site-dependent, is not often a linear relationship with input values, and is related in a complex manner to aqueous concentrations and solubilities. For example, the sensitivity of results in the calcite sub-region depends on the mineral solubilities in the calcite sub-region and on aqueous concentrations passed along from the upgradient siderite sub-region. In turn, the aqueous concentrations in the siderite sub-region depends on the mineral solubilities in the siderite sub-region and on aqueous concentrations passed along from the

upgradient $Al(OH)_3$ sub-region. In this way, a pyramid structure is formed, where a sensitivity test of the sub-region adjacent to the inner core is easily accomplished, but each downgradient sub-region becomes more difficult to test. In addition, Morin (1983) was hampered by the single-value solubility restriction of ADNEUT1 and ADNEUT2: when a solubility was changed for one sub-region, it was changed for all sub-regions. This greatly increased the difficulty of a sensitivity study. However, as ADNEUT3 is not limited to a single-value solubility, the changes caused by varying one solubility product in one sub-region can be evaluated.

Although a complete sensitivity study is not attempted here, observations on the effects of varying relevant solubility products in sub-regions in Area A will be discussed. The input (inner core) solution for the study is listed in Table 1. The sensitivity to other input parameters, such as velocity, can be found in Morin (1983) and Morin and Cherry (in prep, A). It is emphasized again that a sensitivity study is site-dependent and, thus, the following may reliably apply only to Seepage Area A at the Nordic Main impoundment.

The sensitivity of results in the $Al(OH)_3$ sub-region to changes in solubility will be examined first. By changing the log SP (solubility product) of gypsum of -4.63 by +0.10, total calcium increases by 23%, total sulfate increases by 2% (or by an equal molar amount as calcium), and ionic

strength increases by 1.5%; all other concentrations remain essentially constant, including pH and pe. This change in gypsum produces no change in the retardation factor of the $Al(OH)_3$ sub-region, but the consumption of gypsum in the sub-region during each time step doubles. By changing the log SP $Al(OH)_3$ of -32.11 by -1.0, total aluminum decreases by almost one order of magnitude and the migration rate (retardation factor) of the $Al(OH)_3$ sub-region decreases by about one order of magnitude.

The sensitivity of results in the siderite sub-region to changes in solubility is now examined. When all conditions in the $Al(OH)_3$ sub-region remain constant and the log SP $Al(OH)_3$ of -33.61 in the siderite sub-region is changed by +0.5, equilibrium pH of the siderite sub-region increases by 0.02 pH units, pe decreases by 0.05 units, and aqueous concentrations change by less than 1% except for DIC which decreases by about 7% and aluminum which increases by 45%. Also, the retardation factor (migration rate) of the siderite sub-region decreases by about 15%. These variations were also tested for changes in the log SP $Al(OH)_3$ of -33.61 by +1.0 and +1.5 in the siderite sub-region. Results are:

del in log SP $Al(OH)_3$	del in pH (units)	del in pe (units)	del in DIC (%)	del in Al (%)	del in Retard Fact (%)
+0.5	+0.02	-0.05	-7	+45	-15
+1.0	+0.05	-0.10	-19	+125	-38
+1.5	+0.14	-0.33	-41	+277	-80

In addition, the variation of log SP $Al(OH)_3$ in the siderite sub-region causes a minor but noticeable change in characteristics of the calcite sub-region, especially for values of pe, Fe, and the retardation factor.

The sensitivity of results in the calcite sub-region to changes in solubility is now examined. When all conditions in the $Al(OH)_3$ and siderite sub-regions remain constant and the log SP $Al(OH)_3$ of -33.61 in the calcite sub-region is changed by +1.0, equilibrium pH of the calcite sub-region increases by 0.01, pe decreases by 0.21, and all other aqueous concentrations remain essentially constant except Al which increases by 43% and Fe which decreases by 2.5%. The retardation factor of the calcite sub-region is essentially unchanged by the change in $Al(OH)_3$.

In the case where conditions in the $Al(OH)_3$ sub-region remain constant and the log SP $Al(OH)_3$ of -33.11 in the siderite sub-region is changed by +1.0 and log SP $Al(OH)_3$ of -33.61 in the calcite sub-region is changed by +1.0, the following effects on the calcite sub-region are observed: equilibrium pH increases by 0.01, pe decreases by 0.02, Fe increases by 4.5%, Al increases by 43%, and the retardation factor decreases 4%. Comparing these results with results in the two preceeding paragraphs leads to the conclusion that changes in $Al(OH)_3$ solubility cause noticeable changes in some characteristics of sub-regions.

In the case where conditions in the $Al(OH)_3$ and siderite sub-regions remain constant and log SP siderite is -9.34 in the calcite sub-region and log SP calcite of -9.98 in the calcite sub-region is changed by +0.25, equilibrium pH increases by 0.09 units, pe decreases by 0.33 units, ionic strength decreases by 39%, Fe decreases by 60%, Ca decreases by 15%, Al decreases by 7%, SO_4 decreases by 45%, DIC increases by 4%, and the retardation factor increases by 283%. Also, Morin (1983) found that when log SP siderite is -10.34 in the calcite sub-region and the log SP calcite of -10.38 is changed by +1.0, equilibrium pH increases by 0.40 units and the retardation factor increases by 10%. The two cases in this paragraph highlight some of the difficulty of quickly finding precise solubility values which represent well the calcite-siderite solid solution in the calcite sub-region. In addition, using one value for siderite solubility and one value for calcite solubility will never allow a proper representation of the calcite-siderite solid solution.

In addition to the above cases, more complex cases were tested for sensitivity to solubilities. For example, the case in the previous paragraph where log SP calcite of -9.98 was changed by +0.25 was combined with a change of log SP $Al(OH)_3$ of -32.61 by -1.5 in the calcite sub-region. The results are as follows (the results of only changing log SP calcite are repeated in parentheses). Equilibrium pH in-

creases by 0.03 units (increases by 0.09), pe increases by 0.08 units (decreases by 0.33), ionic strength decreases by 6% (decreases by 39%), Fe decreases by 19% (decreases by 60%), Ca increases by 30% (decreases by 15%), Al decreases by 40% (decreases by 7%), SO_4 decreases by 7% (decreases by 45%), DIC increases by 4% (increases 4%), and the retardation factor increases by 14% (increases by 283%).

As was mentioned earlier and is obvious from these sensitivity tests, changes in sub-region characteristics cannot be easily predicted upon a change in mineral solubilities. To reliably predict the changes in characteristics, an equilibrium transport model such as ADNEUT is required.

4.3 CALIBRATION OF ADNEUT3 TO SEEPAGE AREA A

The results of the sensitivity study and other cases were used to calibrate solubilities so that ADNEUT3 would provide the best match possible to conditions found in Area A over the past 5 years. The input solution in Table 1 and the solubilities in Table 2 provided the results listed in Table 3. The solution in Table 1 is representative of inner-core water found at piezometer M1 adjacent to the impoundment dam (Figure 3); the solubilities in Table 2 are representative of values found in Area A (Morin, 1983).

ADNEUT3 values in Table 3 show a much better match with observed values than those of ADNEUT1. This is simply the result of allowing a different solubility in each sub-region

for each mineral. As Morin (1983) pointed out, no piezometers lie completely within the siderite sub-region and, thus, disagreement in this sub-region is the result of errors in observed as well as predicted values. Disagreements in the calcite sub-region, especially in the retardation factors, are attributed to the unsatisafactory representation of the calcite-siderite solid solution by solubilities for the two end members. Aluminum values are predicted satisfactorily by ADNEUT3; differences between predicted and observed values are attributed to the fact that allophane precipitation is not simulated by ADNEUT. Allophane (an amorphous alumino-silicate) is apparently precipitating through most of Area A and is probably capable of removing up to a few millimoles of Al per liter (Morin, 1983).

Using values in Table 1 and 2, which simulate well conditions observed over the past five years in Area A, longer simulations were made. First, simulations representing plume development from its beginning to the present were made. Then simulations predicting plume migration into the future were made.

4.4 DEVELOPMENT OF PRESENT CONDITIONS IN SEEPAGE AREA A

Accurate simulation of the development of present conditions in Area A requires knowledge of the time when acidic seepage began, past hydrologic conditions, the location of the source area of the plume, and the past chemical composi-

tion of inner-core water. None of this information is reliably known for Seepage Area A.

Acidic seepage is believed to have started sometime after draining of ponded water on the surface of the Nordic Main tailings in the late 1960's, which allowed atmospheric oxygen to reach pyrite and initiate acid production. During the draining of the ponded water, hydraulic gradients and groundwater velocities in the tailings and beneath the dam were probably larger than current values.

Morin (1983) attempted to locate the source area of the plume in Area A by installing piezometers in the Nordic Main tailings near and below the tailings-aquifer interface. However, none of the piezometers intersected the source area. Alternatively, by using groundwater flux calculations, solid-paste pH's, aqueous pH's, water table maps, and comparisons of plume and tailings water analyses, Morin (1983) found that the source area probably lies very close to the impoundment dam and may have a cross-sectional area (in the horizontal plane) as small as 3m x 3m. In addition, the source area was suspected to be in the vicinity of piezometer T8-B (Figure 3) based on water analyses, although other locations along the dam could not be reliably ruled out. If the source area indeed lies near T8-B, calculations indicate that the plume moved 2 to 3 times faster in the past if the seepage began in the late 1960's. This higher rate of movement could be the result of higher groundwater

velocities during draining and/or lower-pH, higher-iron water in the inner core; there is some suggestion that the inner core has been decreasing in acidity and cross-sectional area with time (Morin, 1983). These hypotheses for the time when acidic seepage began, higher velocities in the past, the location of the source area, and the past chemical composition of the inner core are evaluated in this section.

To test these hypotheses, three simulations were made and compared to present conditions. One simulation uses present inner-core water with the source area about 30m from M1 near T8-B and velocities under the dam an average of 2.5 times higher than at M1 (Figure 10). The second simulation uses present inner-core water with the source area about 6m from M1 and velocities under the dam equal to those at M1 (Figure 11). The third simulation is similar to the second, but uses more-acidic inner-core water for the first 7 years and then changes to present inner-core water (Figure 12).

Figure 9 is the scenario envisioned for the plume by Morin (1983). The streamtube marked on Figure 9 as "Approximate extent of acidic water" was divided into 14 cells as indicated in Figure 10. The lengths of cells in Area A near the dam were chosen to approximate the existing piezometer spacing; because the groundwater velocity is known in this region, the Residence Time for the simulation (2.5 days) was set. Then the lengths of cells from T8-B to M1 were chosen so that an overall velocity of 2.5 times the value currently

observed at M1 was simulated, thereby representing the higher velocities that are suspected to have existed in the past. Total simulated time was 12 years.

The results of this first simulation for every one-year period are presented in Figure 10. The dashed lines on the first few profiles are the hand-calculated positions of the calcite sub-region (equilibrium pH = 5.7); the best-match retardation factor of ADNEUT3 is about 3.5 times greater than the observed retardation factor for the calcite sub-region (Table 3) and, thus, ADNEUT3 simulates the migration of this sub-region at too high a rate. This problem does not affect in any way the remainder of the simulation.

This first simulation as well as the others discussed in this section indicate that the calcite sub-region migrates out of the simulated streamtube within 3 years. As the calcite sub-region was observed near M18 in 1980 (bottom of Figure 10), this suggests that the plume is less than 3 years old; however, the early simulated profiles do not even approximate the remainder of the observed profile. This contradiction is attributed to the simulation of the calcite-siderite solid solution by end-member solubilities. For example, calcite in the calcite sub-region of Area A is observed to be slowly altering to siderite because of the relatively high concentrations of aqueous iron in the sub-region (Morin, 1983). As a result, the equilibrium pH of the calcite sub-region has been decreasing through the years

(Morin and Cherry, in prep, B), giving the appearance that the calcite sub-region is migrating quickly. In addition, as equilibrium pH decreases, the migration rate of the calcite sub-region decreases until all conditions blend with those of the siderite sub-region. This solid-solution effect cannot be simulated by ADNEUT3. This error only affects simulation of the calcite sub-region and in no way alters the behavior of the remaining sub-regions.

Figure 10 indicates as expected rapid migration under the dam where groundwater velocities are relatively high; as the plume enters Area A, migration rates decrease because groundwater velocities (cell lengths) decrease. Comparison of simulated Year 12 and observed profiles indicate that the observed profile represents greater than 12 years migration under the conditions of this simulation. Extrapolation of simulated results indicate that the observed location of the siderite sub-region for 1980 will be matched after 16 simulated years (4 additional years after Year 12) and the siderite sub-region in 1983 will be matched after 24 simulated years. In other words, 8 simulated years are required to simulate 3 observed years; this indicates input conditions for this simulation are not valid. A similar contradiction is found for the $Al(OH)_3$ sub-region. In addition, if 16 simulated years are required to match the 1980 profile, acidic seepage would have begun in 1964, which appears unlikely.

The second simulation (Figure 11) assumes the source area is only 6m from M1 under the dam; velocities in this short region under the dam are reasonably assumed to be equal to those at M1. Because the source area is closer to M1 than in the previous simulation, the sub-regions have migrated farther through Area A in this simulation after an equal number of simulated years; this in effect will indicate seepage has begun closer to the present time in this second simulation. Comparison of simulated profiles with observed profiles indicate that the 1980 profile is matched well at simulated Year 14; the decision between Years 12, 13, and 14 is based on the use of cell patterns as discussed above in Section 3.2. The 1983 profile would be best matched by Simulated Year 19. Thus, 5 simulated years are required to simulate 3 observed years; this is a satisfactory match considering the discretization of the streamtube and the lengths of cells, yet additional details will be addressed under the third simulation. Because the observed 1980 profile is matched well by Year 14, this would indicate that acidic seepage began around 1966 which is somewhat earlier than expected.

The third simulation (Figure 12) is identical to the second, except the input solution of Table 4 was used for the first 7 years; this solution is typical of the somewhat more-acidic water found in the tailings. Figure 12 shows that the siderite and $Al(OH)_3$ sub-regions have nearly iden-

tical equilibrium pH's, 5.27 and 5.31 respectively; they are separated by a dot on Figure 12. Because the $Al(OH)_3$ sub-region has a higher equilibrium pH, the sub-region order from the inner core is: inner core, siderite sub-region, $Al(OH)_3$ sub-region, and calcite sub-region. The solution of Table 4 produces a slightly faster migration rate than the solution of Table 1 for the sub-region adjacent to the inner core. After the solution in Table 1 begins to enter the streamtube after 7 years, the sub-regions are re-ordered and a profile typical of Figures 10 and 11 begins to develop; however, because the sub-regions begin to develop after Year 7, they are not as long by Year 15 as found on Figures 10 and 11.

Comparison of simulated and observed profiles indicates that the 1980 profile is matched satisfactorily around Year 13 and 14, suggesting acidic seepage began in 1966-1967; however, the length of the $Al(OH)_3$ sub-region should be longer than simulated. To obtain the proper length, the present inner-core solution should simply enter the streamtube after a shorter amount of time, i.e. after about 3 years. A satisfactory match for the 1983 profile would be obtained around Year 17, although the simulated $Al(OH)_3$ sub-region should again be longer. Because 3 observed years are simulated by 3 to 4 simulated years, this simulation uses the most valid input conditions of the simulations in this section.

In summary, by using ADNEUT3, it has been found that 1) acidic seepage probably began leaving the tailings impoundment around 1966-1967, 2) the source area is very close to M1 at the impoundment dam and, as a result, past hydrologic conditions under most of the dam are not important, and 3) the initial chemical composition of the inner core was probably more acidic than the present composition for a short period of time. Such cases as more-acidic water at T8-B producing a migration rate 2 to 3 times the current rate can also be ruled out by the results of the simulations in this section.

4.5 PREDICTIONS OF FUTURE CONTAMINANT MIGRATION IN SEEPAGE AREA A

This section examines possibilities of future contaminant migration in Seepage Area A. Because all simulations in the previous section (Figures 10, 11, and 12) indicate that the inner core reached piezometer M1 around 1970, all simulations in this section begin in 1970 at M1. Because of the variation in velocity over a distance of 240m from the dam, 26 cells are used to obtain sufficient detail while maintaining a reasonable number of time steps. The residence time for each cell is 58.5 days.

Figure 13 is the first long-term simulation (see also Figure 3 for piezometer locations); input values are the data in Tables 1 and 2 with an initial calcite content of 0.85 wt-% for each cell. As with Figures 10 to 12, the

dashed lines in the first few profiles represent the hand-calculated position of the calcite sub-region using the observed retardation factor. Figure 13 indicates that the sub-regions initially migrate quickly from the dam because of the higher velocities and migration is barely perceptible far from the dam where velocities are low. The Seepage Collection Ditch, which actually collects only a small portion of the seepage for $BaCl_2$ treatment, is the first important destination in contaminant migration. The siderite sub-region (pH = 5.3) reaches the Ditch in a relatively short time; the $Al(OH)_3$ sub-region reaches the Ditch after 325 years (2295 A.D.); and the inner core reaches the Ditch after 500 years (2470 A.D.). The $Al(OH)_3$ sub-region would reach the end of the simulated streamtube at 240m after about 1050 years (3020 A.D.) and the inner core would reach the end after 1625 years (3595 A.D.).

If input data are reasonable for conditions both close to and far from the dam, these predictions indicate that on an absolute scale the contaminant plume in Area A will not cause extensive environmental contamination over a few thousand years. However, during this span of years, input conditions may change as a result of man-made or natural effects. As examples of man-made changes, the Seepage Collection Ditch might be deepened to intercept a greater percentage of the seepage, the Nordic Main tailings may be covered with impermeable material causing a change in hy-

draulic gradients in the aquifer, or a water reservoir might be built to the east of Area A causing a change in direction of hydraulic gradients so that the plume turns to the west towards the $BaCl_2$ treatment plant. The effects of these changes can be evaluated by available finite-element or finite-difference models.

Examples of possible natural changes are the decrease in the rate of pyrite oxidation and acid production, which can be examined by ADNEUT3, and natural changes in groundwater velocities, which would probably not be significant. Figure 14 indicates the effect of a dilute solution (Table 5), with a pH of 4.0 reflecting the acid-rain pH in this region, flowing through the streamtube. This results in only one sub-region, the calcite sub-region with an equilibrium pH of 6.96, and inner-core migration is much more retarded than observed for the present-day inner-core solution. A similar effect would eventually result if this solution began entering the streamtube of Figure 13 after any length of time. Such a scenario would represent the cessation of acid production at the source area and the introduction of unaltered infiltrating precipitation, which is likely to happen sometime in the future.

Figure 15 represents the intermediate step that would probably occur between cessation of acid production and the introduction of unaltered precipitation into the streamtube. Because the Nordic Main tailings contain a large amount of

gypsum, a solution at gypsum saturation such as in Table 6 (Dubrovsky, personal communication) would probably enter the streamtube for some time before the unaltered precipitation appeared. Figure 15 shows the effect of this solution 25 years after its introduction into the streamtube (Year 175): chemical perturbations are created until equilibrium with the new solution is re-established in all sub-regions. There is a calcite sub-region (pH = 5.68) with no siderite created by the relatively high concentrations of aqueous calcium. There is also a small perturbation of pH 5.9 where siderite created by the first input solution temporarily co-exists with the newly formed calcite. This simulation covers only 175 years because of greatly increased execution costs for calculation of re-equilibrium and chemical perturbations; nevertheless, within another 50 years (Year 225), complete re-equilibrium would probably be attained throughout the streamtube and only two sub-regions would then exist: calcite (pH = 5.68) and $Al(OH)_3$ (pH = 5.19). The migration rates of these sub-regions are less than those produced by the present-day input solution.

In summary, two scenarios for future contaminant migration have been examined in detail in this section. The first scenario (Figure 13) assumes all input conditions (Table 1 and 2) remain constant. The results of this simulation indicate that hundreds of years are required for the sub-regions to migrate over 100 meters from the dam. The

second scenario assumes acid production in the tailings ceases, then a dilute gypsum-saturated solution enters the streamtube after some time, and finally unaltered infiltrated precipitation enters the streamtube. The results of this scenario (a combination of Figures 13, 14, and 15) indicate transient chemical perturbations are created and the migration rates and numbers of sub-regions decreases as each successive solution enters the streamtube. As a result, Figure 13 describes the mostly likely worst-case scenario. In the unlikely event acid production increases, migration rates will be greater than those of Figure 13; the amount of increase in the rates will depend on the exact solution produced. In addition, if increased acid production produces an inner-core pH less than 3, an $Fe(OH)_3$ sub-region may be created.

5. CONCLUSIONS

This study and related past studies have shown that one-dimensional chemical equilibrium-transport models, such as ADNEUT, satisfactorily simulate contaminant migration from uranium-tailings impoundments. For this study, ADNEUT3 was developed from ADNEUT1 to specifically allow variable conditions during a simulation. ADNEUT3 was calibrated to present conditions at a tailings seepage site at the Nordic Main uranium-tailings impoundment near Elliot Lake, Ontario, and ADNEUT3 was then used to identify probable past and future conditions at the site.

Past conditions addressed were 1) the approximate year when acidic seepage began leaving the tailings impoundment at the seepage site (1966-1967), 2) the past chemical composition of the seepage (somewhat more acidic for a short period of time), and 3) the location of the source area within the tailings of the acidic water (near the impoundment dam, close to the seepage site). Future conditions addressed were the migration rates of the acidic water and the effect of decreasing acid production within the tailings on migration rates. Simulations indicated that hundreds of years are required under present conditions for the most acidic water with associated high levels of contaminants to migrate about 100m from the tailings impoundment. The significant neutralization capacity of the aquifer is the primary cause of this relatively slow migration rate. Simulations of future migration also indicated that migration rates of contaminants will decrease if acid production within the tailings decreases.

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Morin,K.A., J.A. Cherry, T.P. Lim, N. Dave, and A.J. Vivyurka. In preparation. Migration and prediction of acidic seepage from uranium-tailings impoundments. 1.Field study and conceptual model of seepage migration.

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Table 1

Input (inner-core) Solution For Seepage Area A Simulations

Values represent the inner core at M1 in Area A

Temperature = 10°C

pH = 4.40 pe = 3.64

(the following values are in moles/liter)

Fe = 9.310E-02	Ca = 1.000E-02	Mg = 1.646E-02
K = 3.197E-03	Na = 6.090E-04	Mn = 7.099E-04
Al = 7.000E-03	SO4= 1.320E-01	Cl = 4.231E-04
F = 1.632E-03	DIC= 8.000E-03	Si = 4.510E-04

Table 2

Solubilities Used To Provide ADNEUT3 Results In Table 3.

Mineral:	cal	sid	gyp	Fe(OH)3	Al(OH)3
sub-reg					
calcite	-9.98	-9.34	-4.63	-37.10	-33.61
siderite	-9.98	-10.34	-4.63	-37.10	-32.11
Al(OH)3	-9.98	-10.34	-4.63	-37.10	-32.71
Fe(OH)3 *	-9.98	-10.34	-4.63	-37.10	-32.71

* = irrelevant because no Fe(OH)3 sub-region exists in Area A

Table 3
Comparison Of Observed, ADNEUT1, and ADNEUT3 Data

(I=inner core, inner-core values are used as input)
(obs=observed value, pred=predicted value)
(concentrations are as millimolar)

	: sub-regions			:
	I	Al	Sid	Calc*
pH obs(1980)	4.40-4.61	4.61-5.20	5.20-5.70	5.70-5.85
(1982)	4.60-5.18	5.18-5.43	5.43-5.21	5.21-5.51
pH pred AD1	4.40	5.20	5.24	5.46(5.93)
pH pred AD3	4.40	5.02	5.27	5.73
Fe obs(1980)	100.8-96.3	96.3-42.5	42.5-39.2	39.2-20.1
(1982)	89.3-83.2	83.2-55.8	55.8-53.8	53.8-43.1
Fe pred AD1	93.1	93.1	95.4	1.0(1.3)
Fe pred AD3	93.1	93.1	94.7	41.6
Ca obs (80)	8.9-8.7	8.7-6.9	6.9-7.9	7.9-11.9
(82)	10.0-10.2	10.2-11.6	11.6-11.4	11.4-11.5
Ca pred AD1	10.0	10.0	10.0	10.5(12.3)
Ca pred AD3	10.0	12.5	12.5	12.6
Al obs (80)	6.9-4.0	4.0-0.8	0.8-0.4	0.4-<0.1
(82)	5.2-2.9	2.9-0.3	0.3-0.3	0.3-<0.1
Al pred AD1	7.4	8.2	6.7	1.1(1.3)
Al pred AD3	7.0	7.3	6.8	0.88
SO4 obs(80)	139.3-120.6	120.6-64.6	64.6-67.2	67.2-47.3
(82)	124.9-116.2	116.2-85.7	85.7-82.4	82.4-71.0
SO4 pre AD1	132.0	132.0	132.0	38.0(29.0)
SO4 pre AD3	132.0	132.0	132.0	71.5
DIC obs (80)	5-10	5-10	5-10	5-10
(82)	5-10	5-10	5-10	5-10
DIC pred AD1	8.0	8.0	10.3	19.0(21.5)
DIC pred AD3	8.0	8.0	9.6	19.5
Ret. Fact. obs		0.27%	0.27%	2-6%
R.F. pred AD1		0.8-0.07	0.58	17.6-14.7
R.F. pred AD3		0.20	0.46	14.0

* = values for the calcite sub-region as predicted by ADNEUT1 are based on the log SP calcite = -2.0 + std log K (and, in parentheses, log SP calcite = -1.0 + std log K)

Table 4

Alternative Input Solution For Simulating Development Of Plume Conditions

Temperature = 10°C

pH = 3.63 pe = 7.00

(the following are in moles/liter)

Fe = 1.807E-01	Ca = 1.000E-02	Mg = 6.914E-02
Na = 3.045E-04	K = 3.197E-03	Mn = 4.375E-05
Al = 7.000E-03	SO4= 2.780E-01	Cl = 4.231E-05
F = 1.632E-03	DIC= 8.000E-03	Si = 4.510E-04

Table 5

Very Dilute Solution

Temperature = 10°C

pH = 4.00 pe = 8.00

(the following are in moles/liter)

Fe = 4.000E-05	Ca = 7.500E-04	Mg = 1.000E-04
Na = 4.000E-04	K = 1.000E-04	Mn = 1.000E-04
Al = 1.000E-05	SO4= 1.200E-03	Cl = 5.000E-04
F = 5.000E-07	DIC= 3.000E-04	Si = 1.000E-04

Table 6

Dilute Gypsum-Saturated Solution (Dubrovsky, personal communication)

Temperature = 10°C

pH = 4.00 pe = 8.00

(the following are in moles/liter)

Fe = 4.118E-05	Ca = 1.338E-02	Mg = 8.642E-05
Na = 3.610E-05	K = 5.371E-05	Mn = 1.820E-06
Al = 4.633E-06	SO4= 1.250E-02	Cl = 2.821E-04
F = 1.000E-06	DIC= 6.325E-03	Si = 1.488E-03

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Figure 14. Predictions of future contaminant migration with a very dilute input solution at pH 4

Figure 15. Predictions of future contaminant migration with a dilute gypsum-saturated solution beginning at Year 150

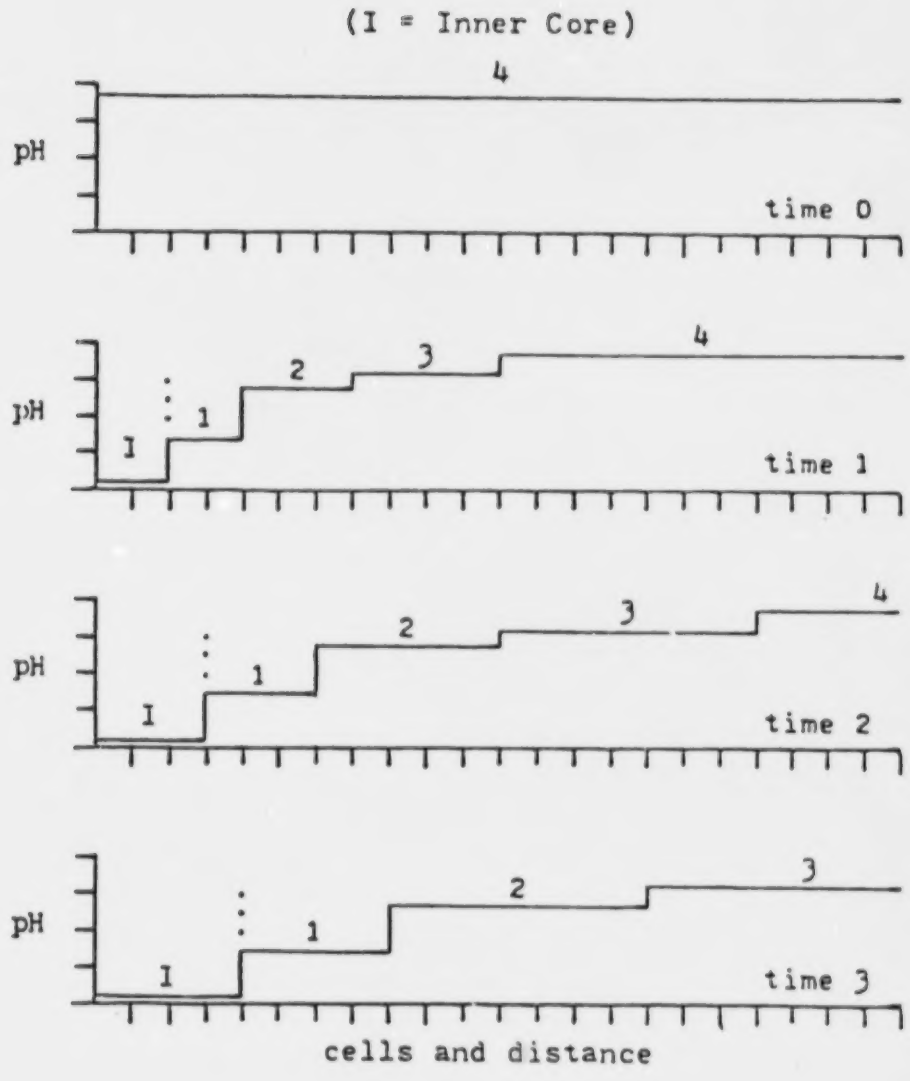

Figure 1. Example of a multi-cell-mode simulation

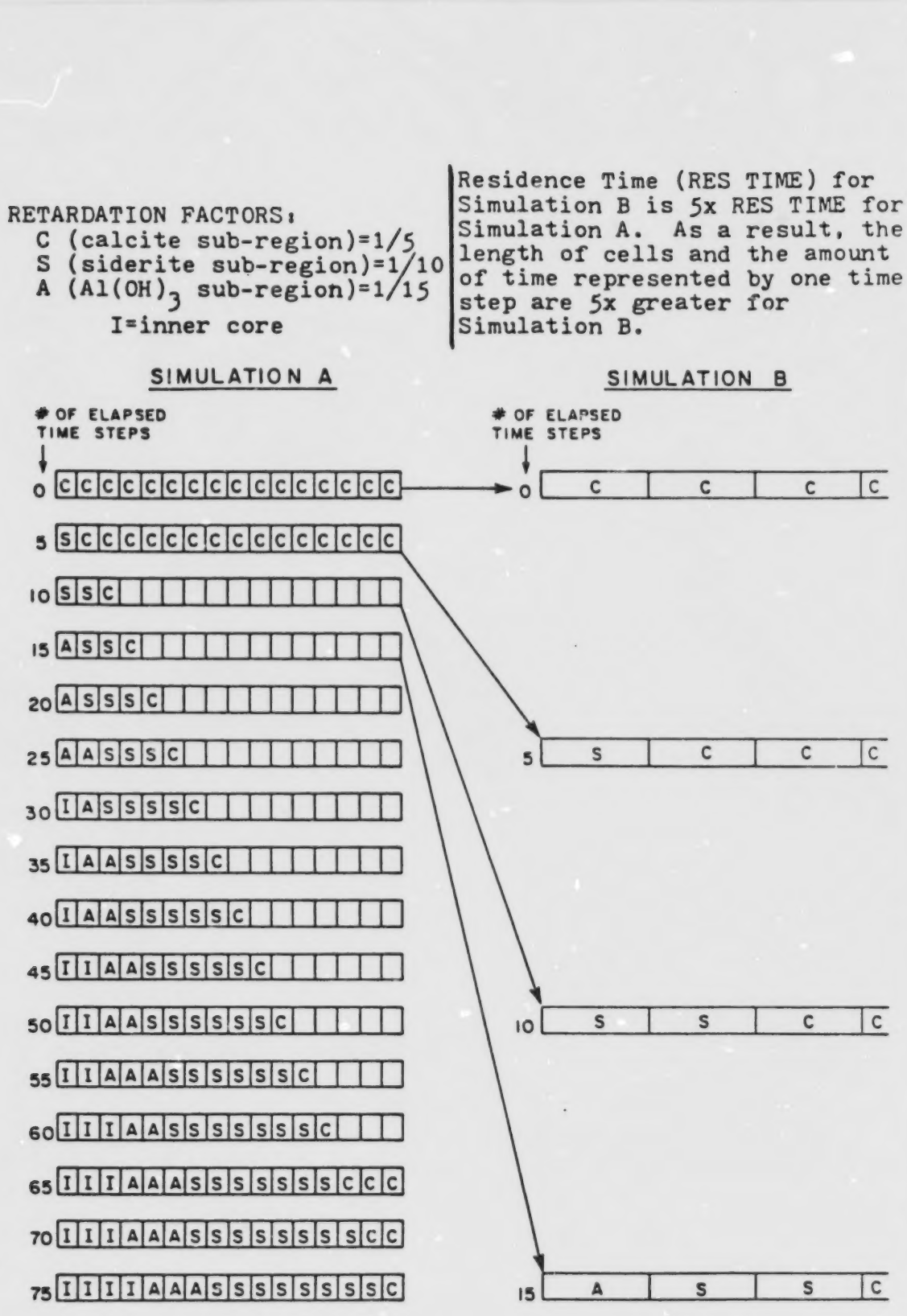
RETARDATION FACTORS:
C (calcite sub-region)=1/5
S (siderite sub-region)=1/10
A (Al(OH)3 sub-region)=1/15
I=inner core
Residence Time (RES TIME) for Simulation B is 5x RES TIME for Simulation A. As a result, the length of cells and the amount of time represented by one time step are 5x greater for Simulation B.
SIMULATION A
SIMULATION B
OF ELAPSED TIME STEPS
OF ELAPSED TIME STEPS
0 C C C C C C C C C C C C C C C C
5 S C C C C C C C C C C C C C C C
10 S S C
15 A S S C
20 A S S S C
25 A A S S S C
30 I A S S S S C
35 I A A S S S S C
40 I A A S S S S S C
45 I I A A S S S S S C
50 I I A A S S S S S S C
55 I I A A A S S S S S C
60 I I I A A S S S S S S C
65 I I I A A A S S S S S S C C C
70 I I I A A A S S S S S S S C C
75 I I I I A A A S S S S S S S C
0 C C C C
5 S C C C
10 S S C C
15 A S S C

Figure 2. Simulation of sub-region migration by a cell model.

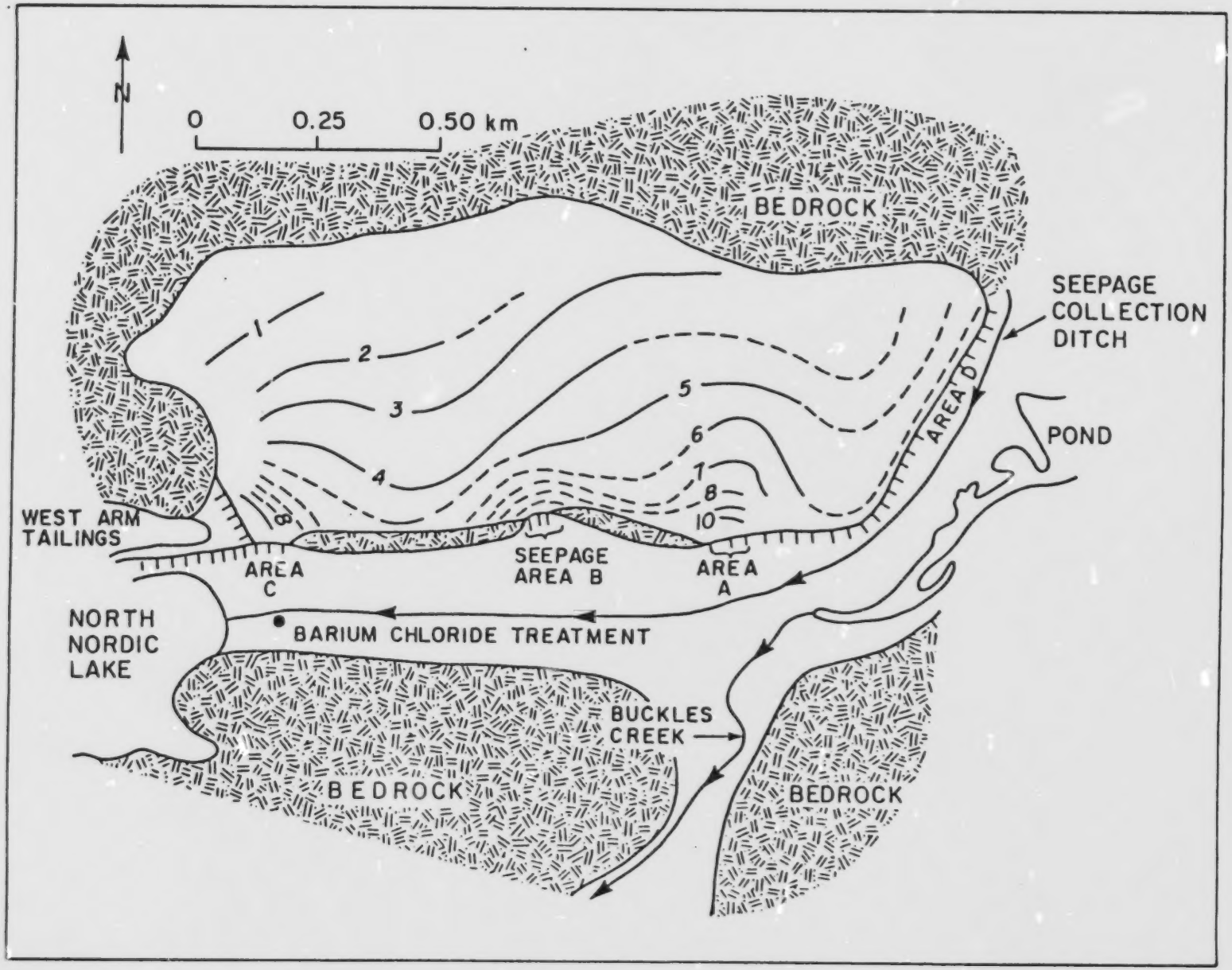

Figure 3a).

Figure 3. Maps of the Nordic Main area

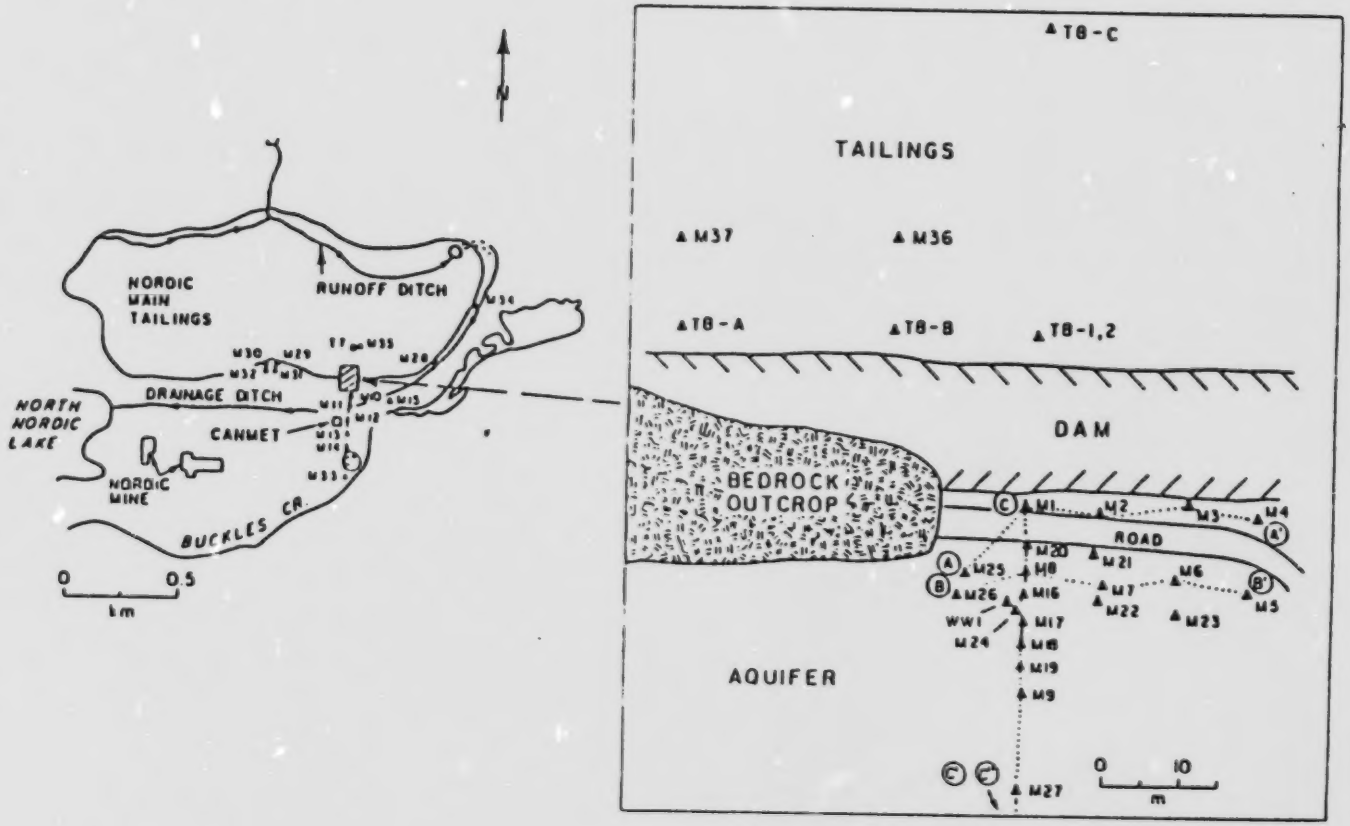
NORDIC MAIN TAILINGS
RUNOFF DITCH
DRAINAGE DITCH
NORTH NORDIC LAKE
CANMET
NORDIC MINE
BUCKLES CR.
0 0.5 km
TB-C
TAILINGS
M37
M36
TB-A
TB-B
TB-1,2
DAM
BEDROCK OUTCROP
ROAD
AQUIFER
WW1
0 10 m

Figure 3b).

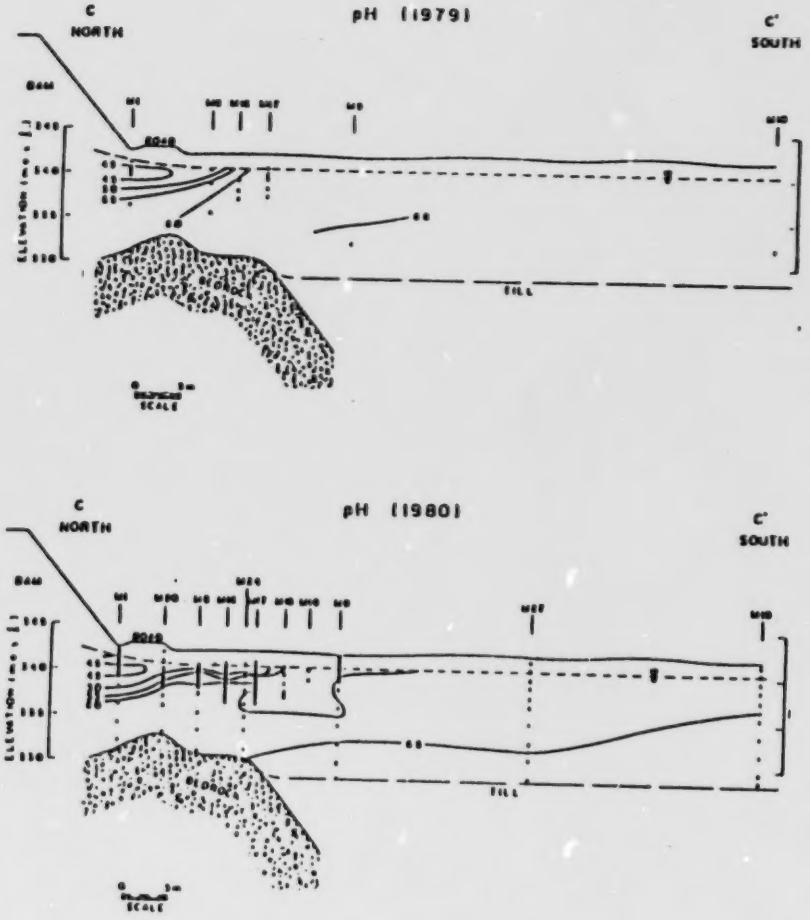

Figure 4. Centerplane profiles for pH

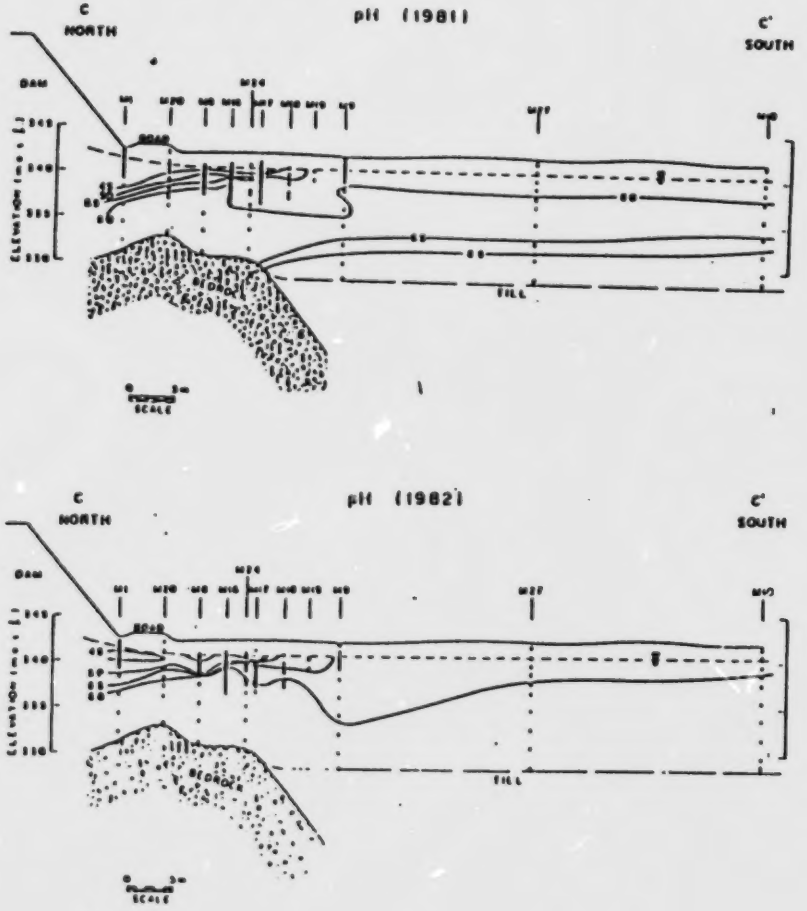

Figure 4 (continued).

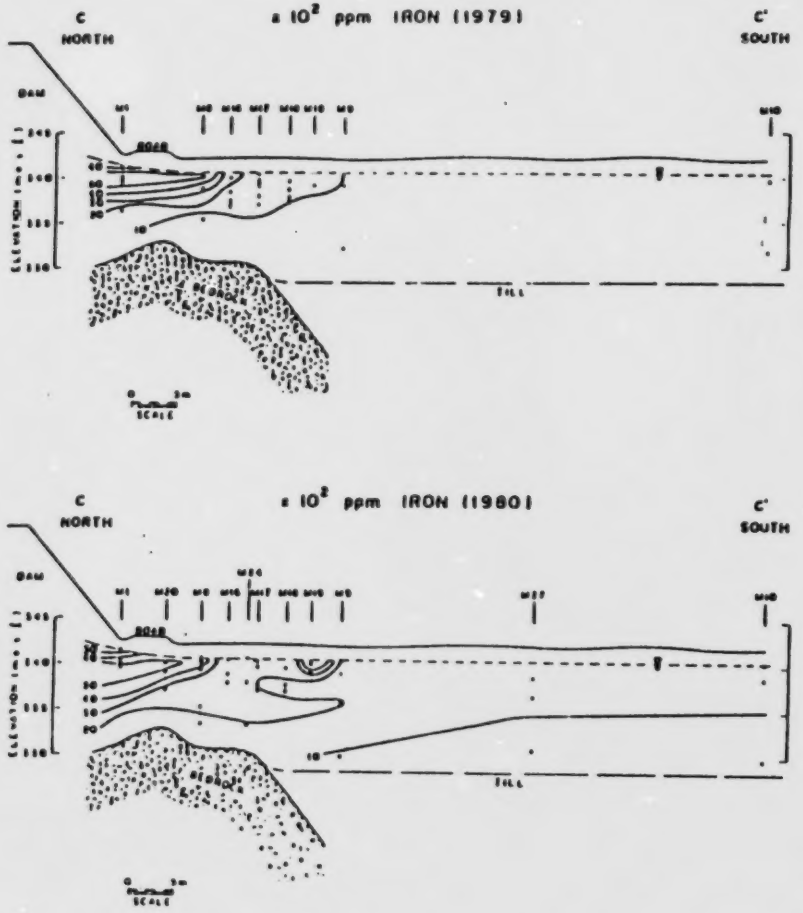

Figure 5. Centerplane profiles for iron

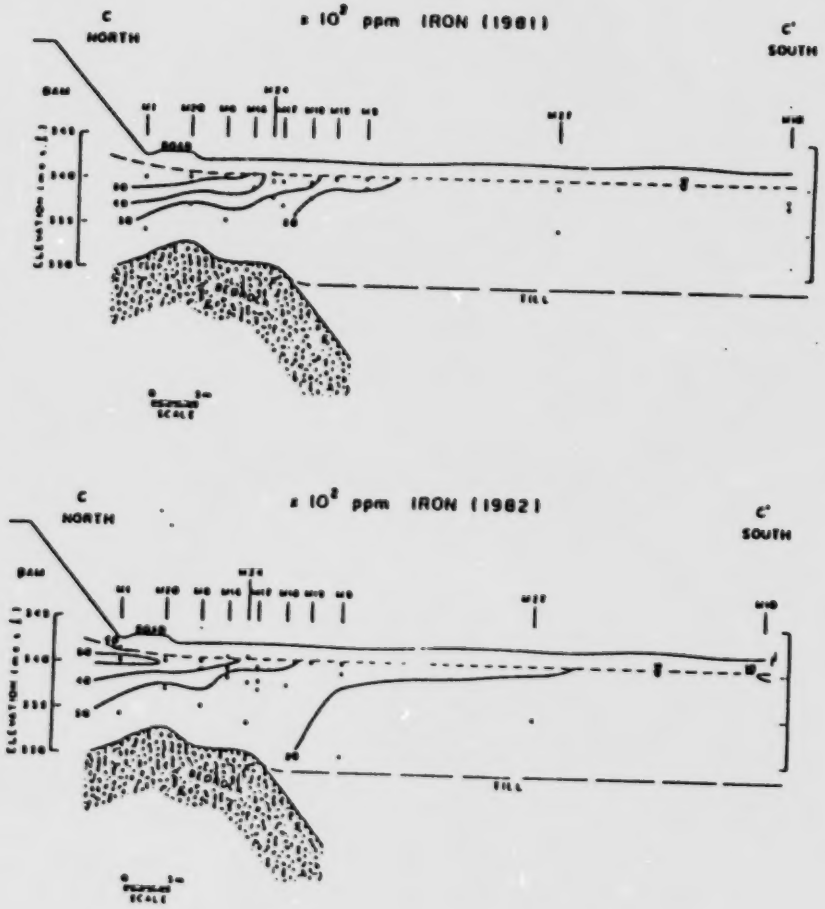

Figure 5 (continued).

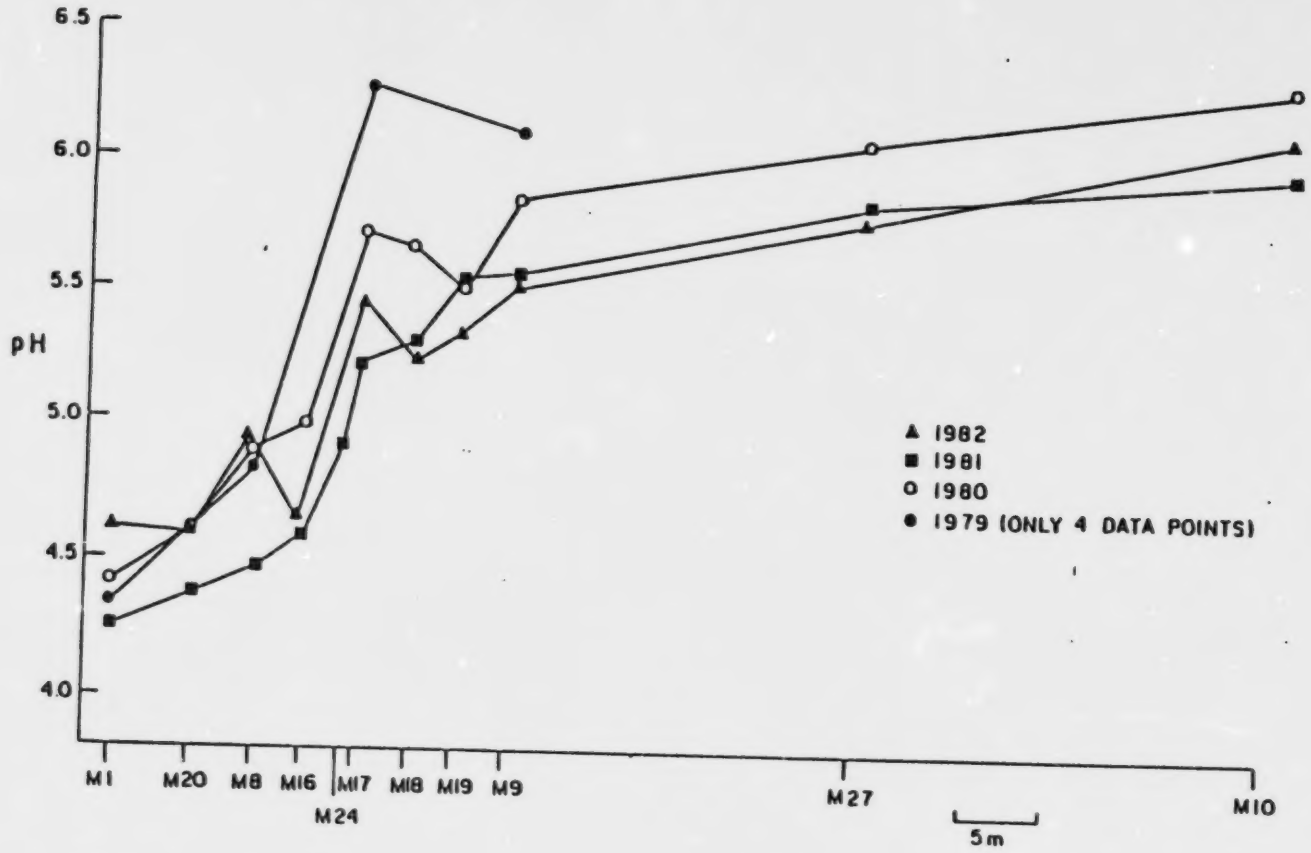

Figure 6. Centerline profiles for pH

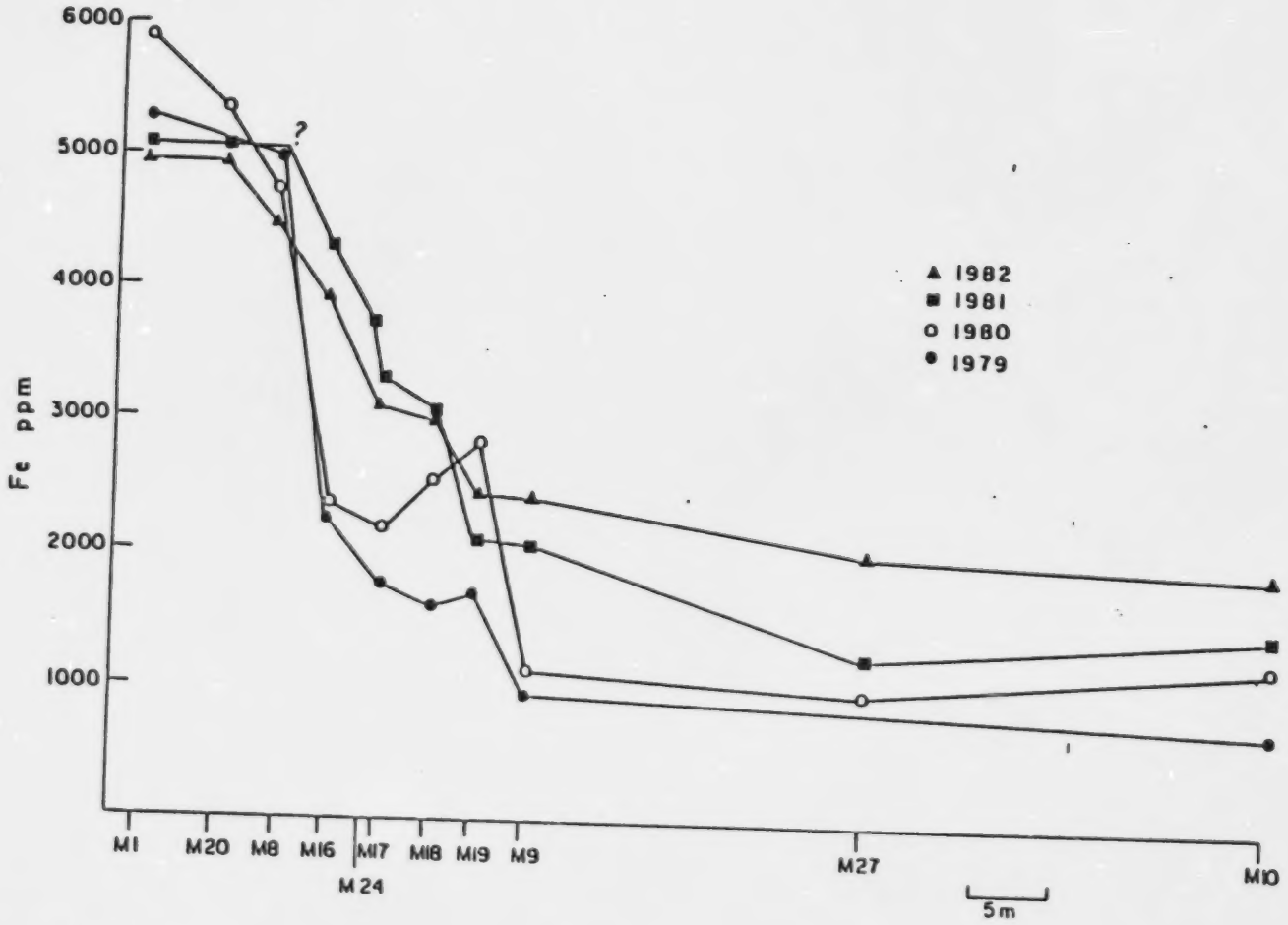

Figure 7. Centerline profiles for iron

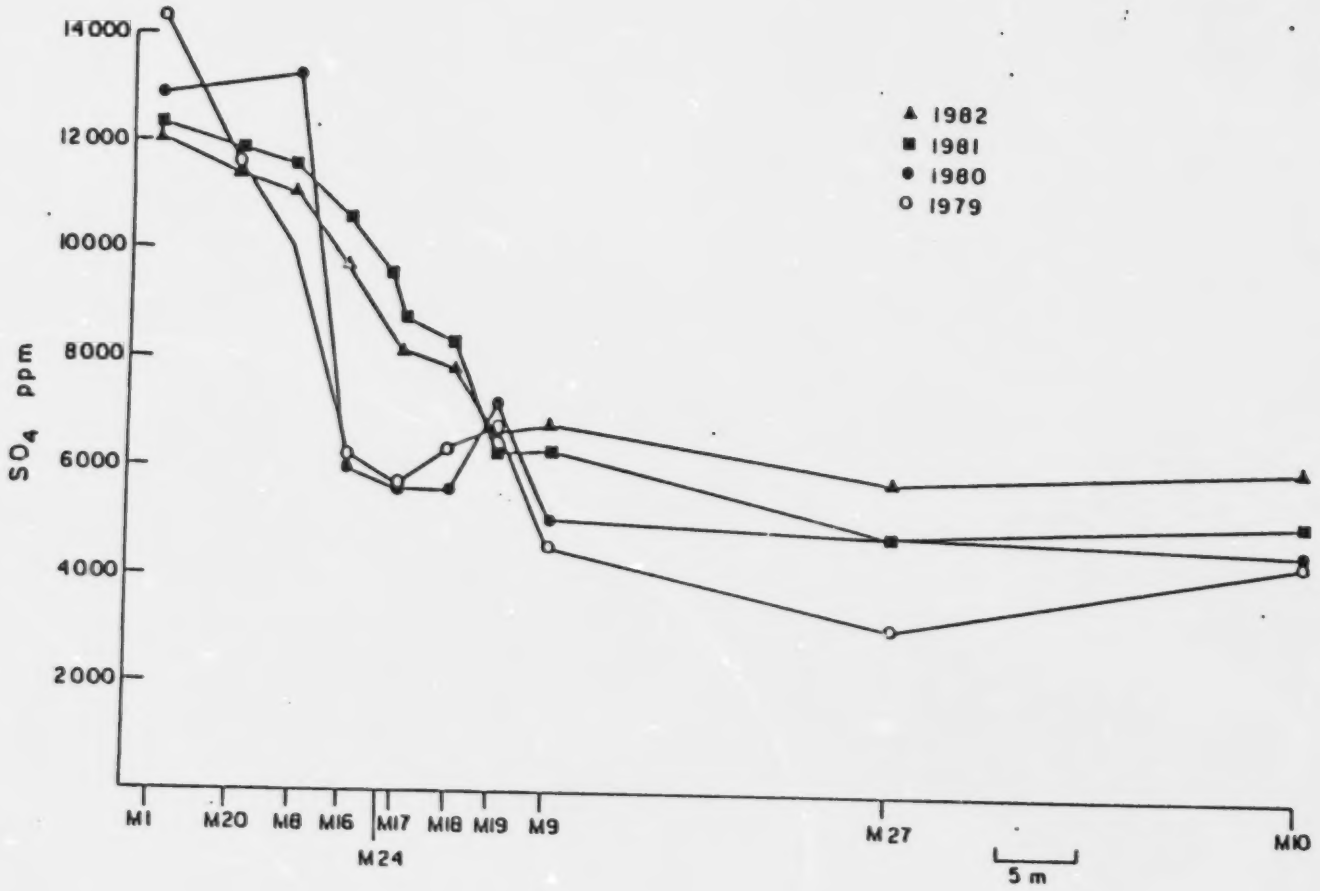

Figure 8. Centerline profiles for sulfate

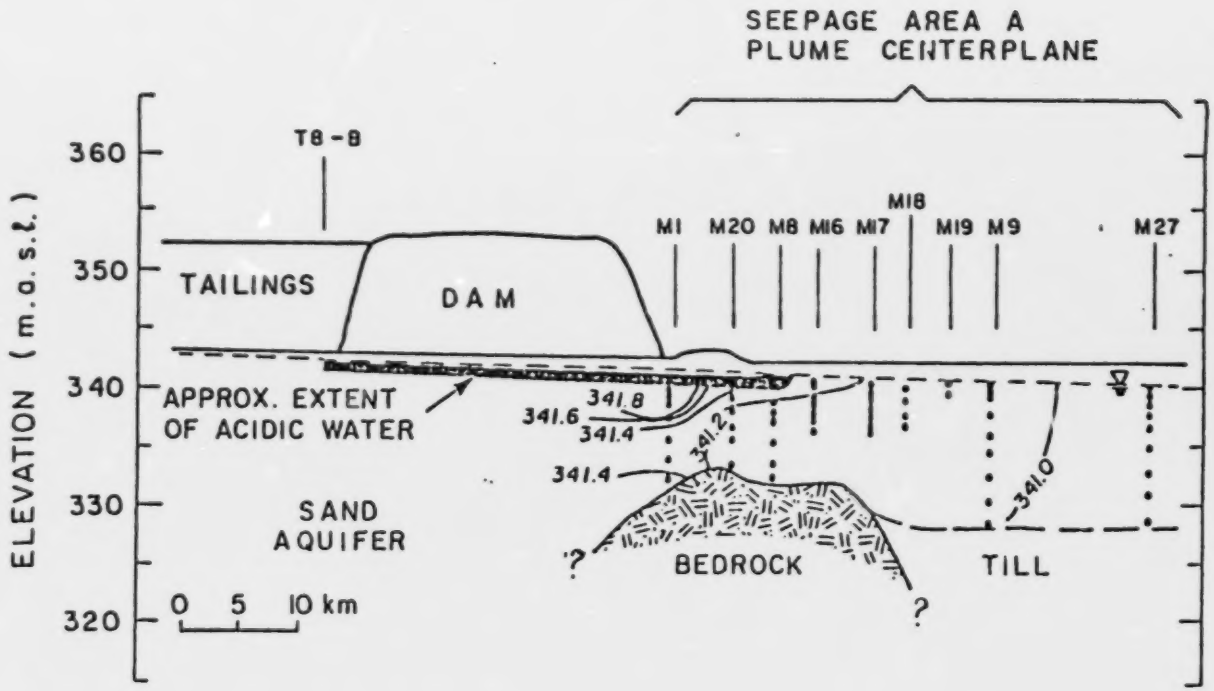

Figure 9. Plume location envisioned in Morin (1983)

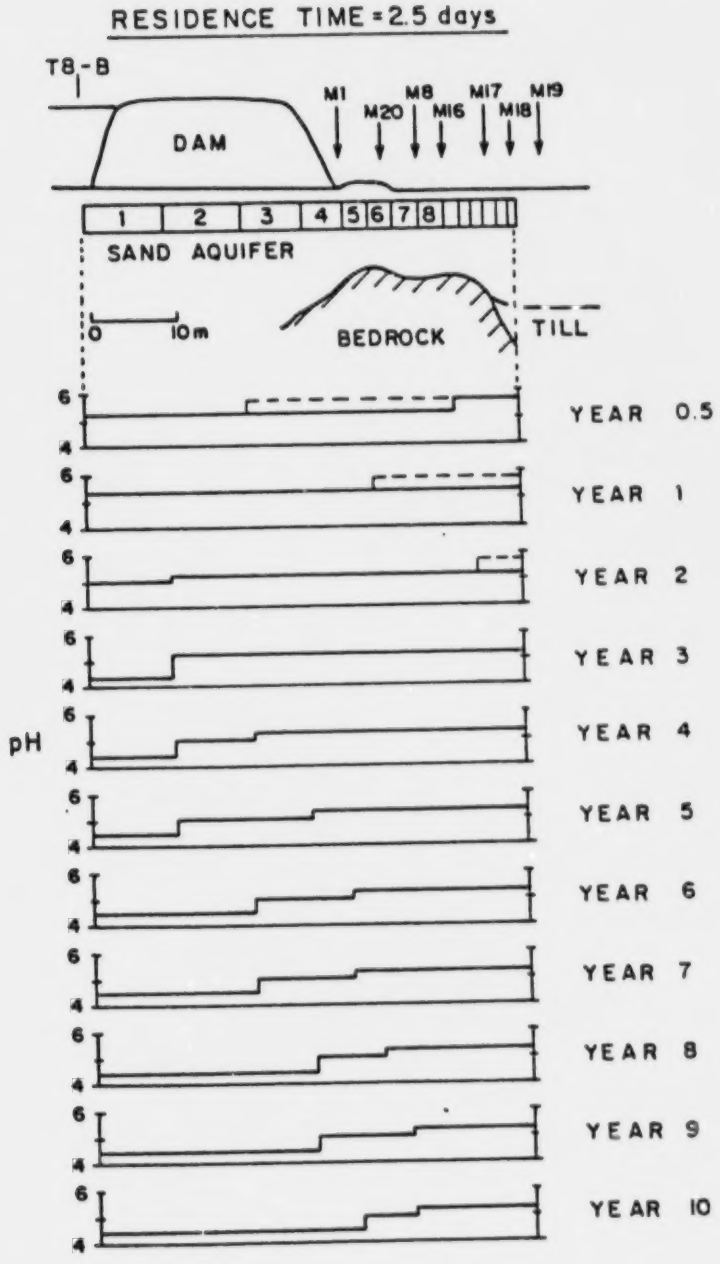

Figure 10. Simulation of plume development from T8-B, 30m from M1. (Dashed lines represent hand-calculated location of the calcite sub-region)

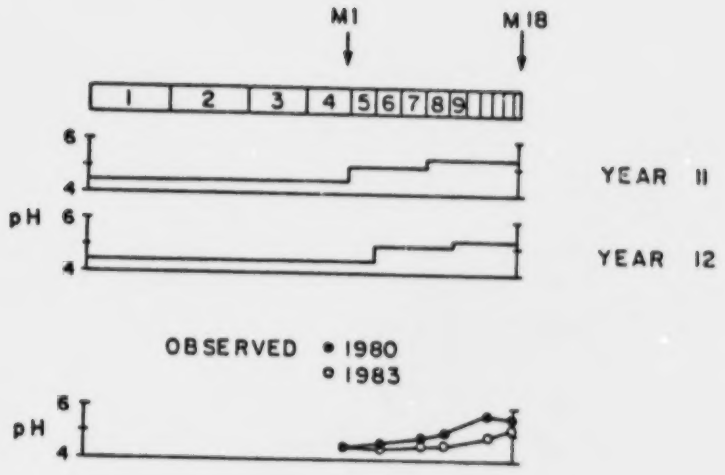

Figure 10 (continued)

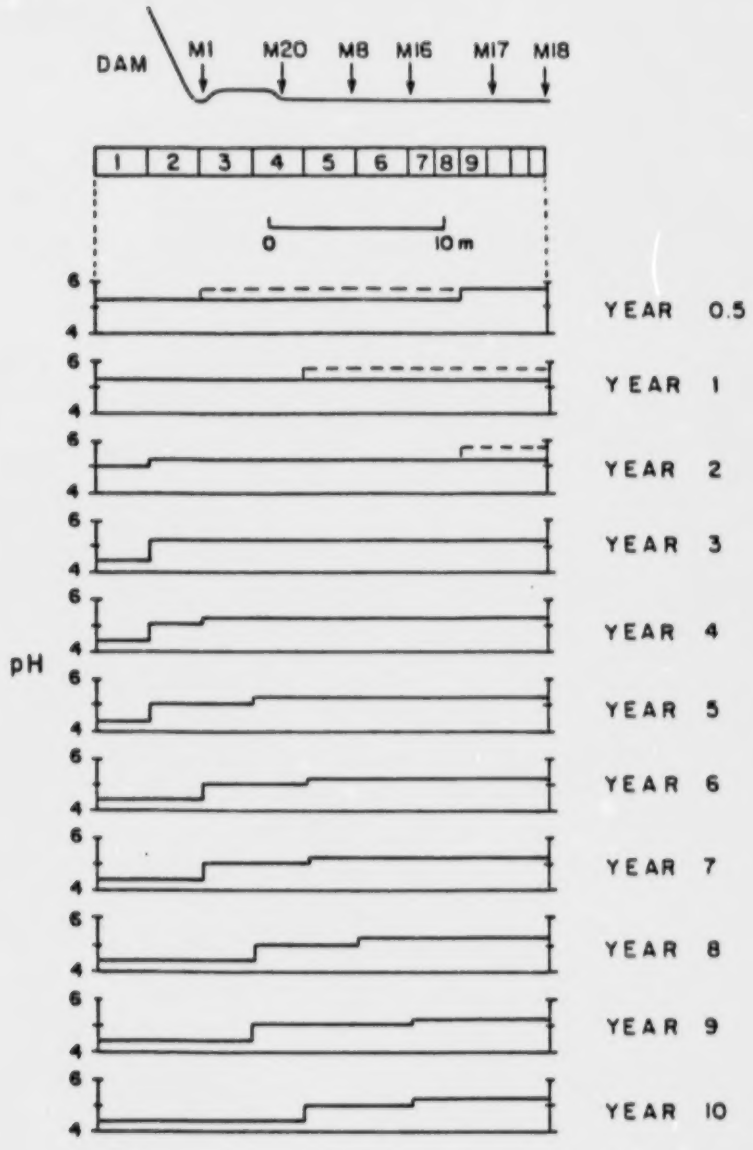

Figure 11. Simulation of plume development from near M1. (Dashed lines represent hand-calculated locations of the calcite sub-region)

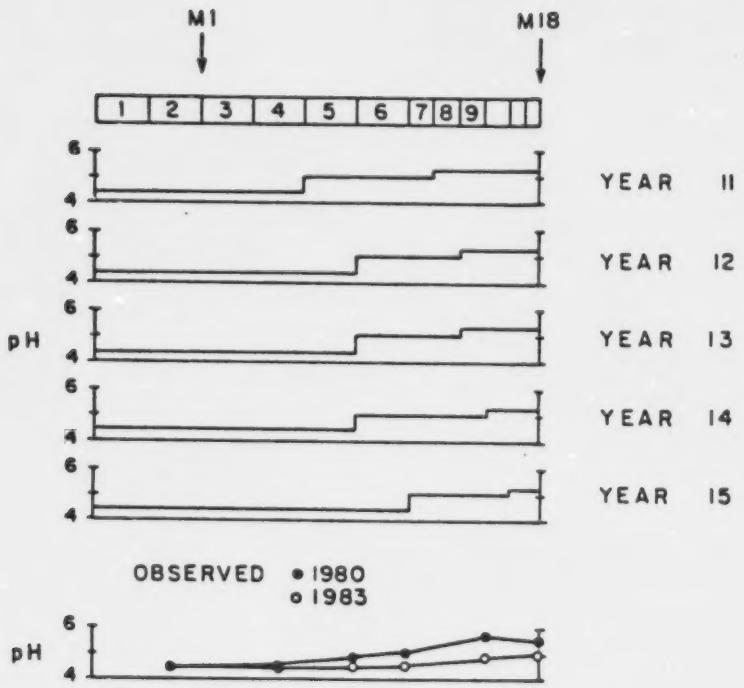

Figure 11 (continued)

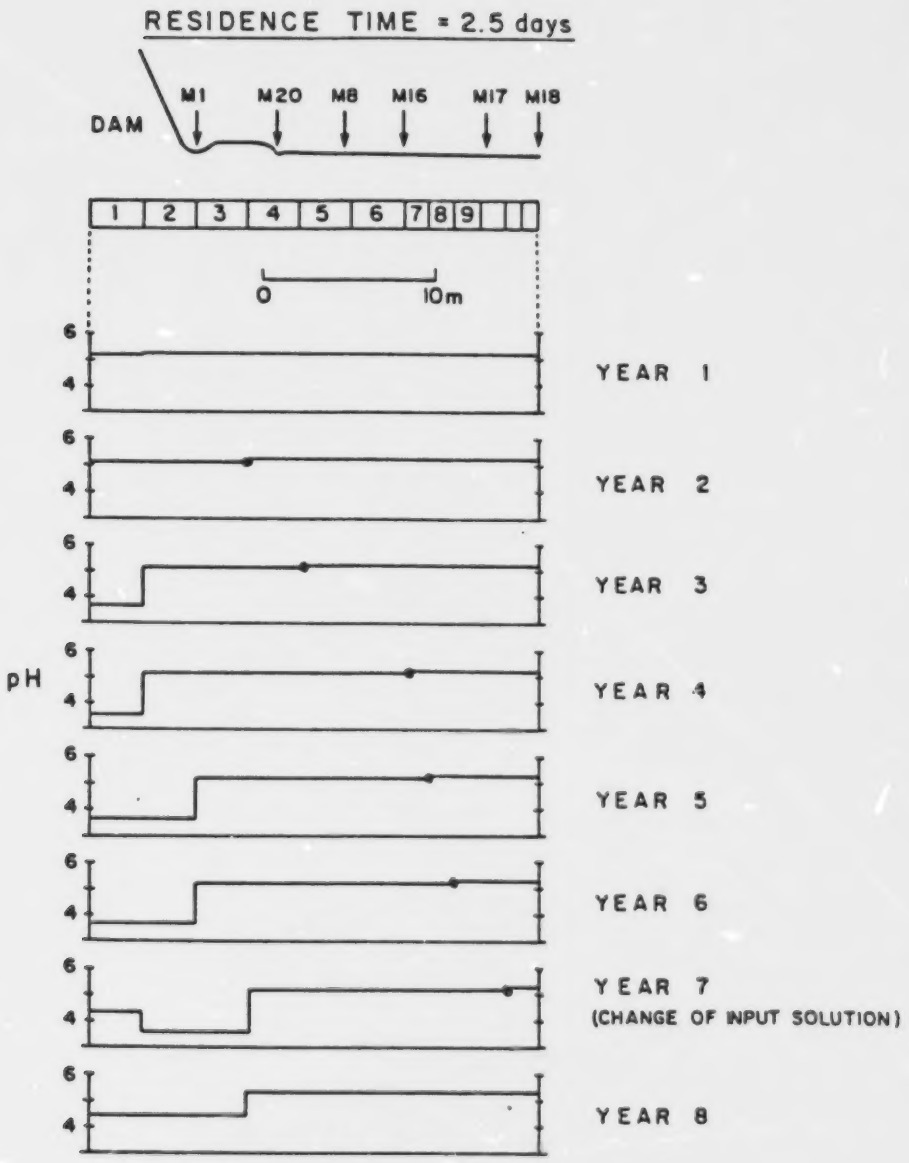

Figure 12. Simulation of plume development from near M1 with more-acidic inner-core water for the first 7 years. (Dots separate two similar sub-regions, see text)

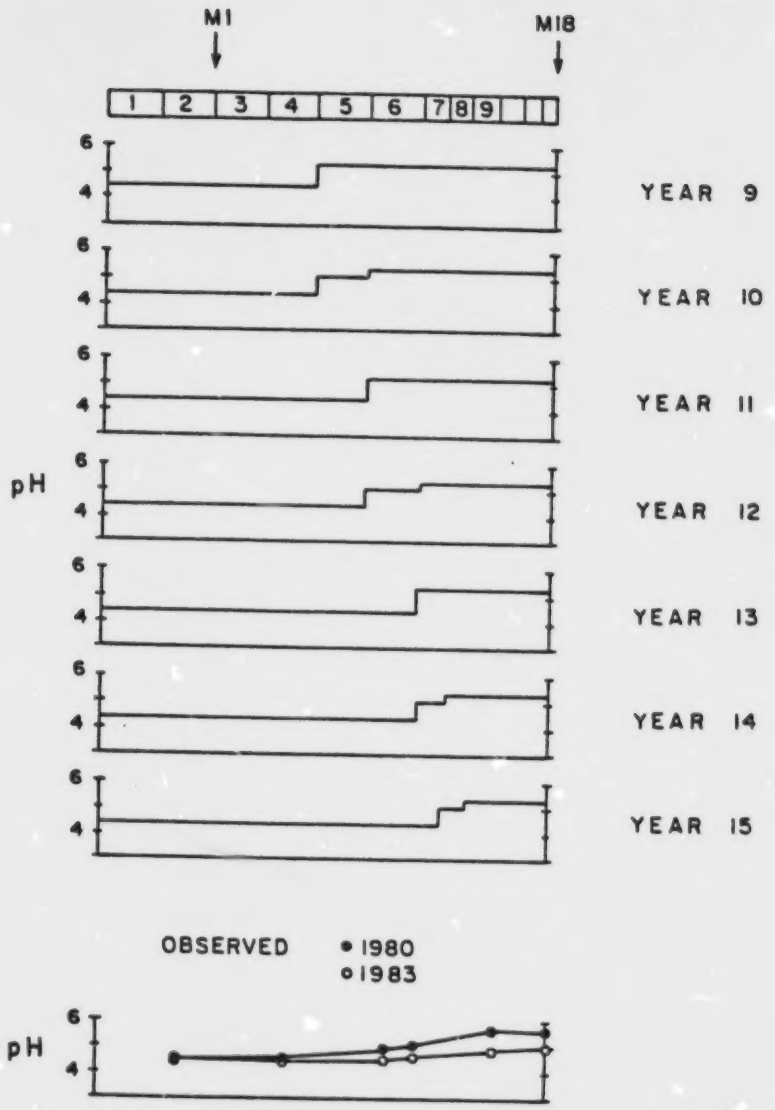

Figure 12 (continued)

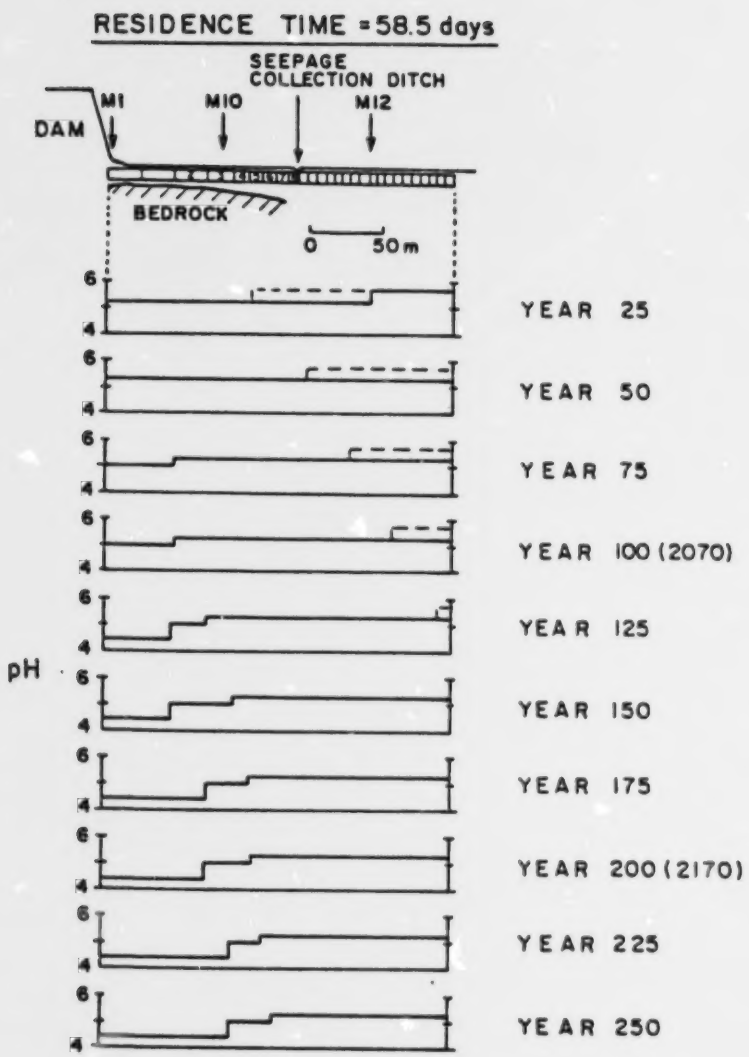

Figure 13. Predictions of future contaminant migration based on constant conditions. (Dashed lines represent hand-calculated location of the calcite sub-region)

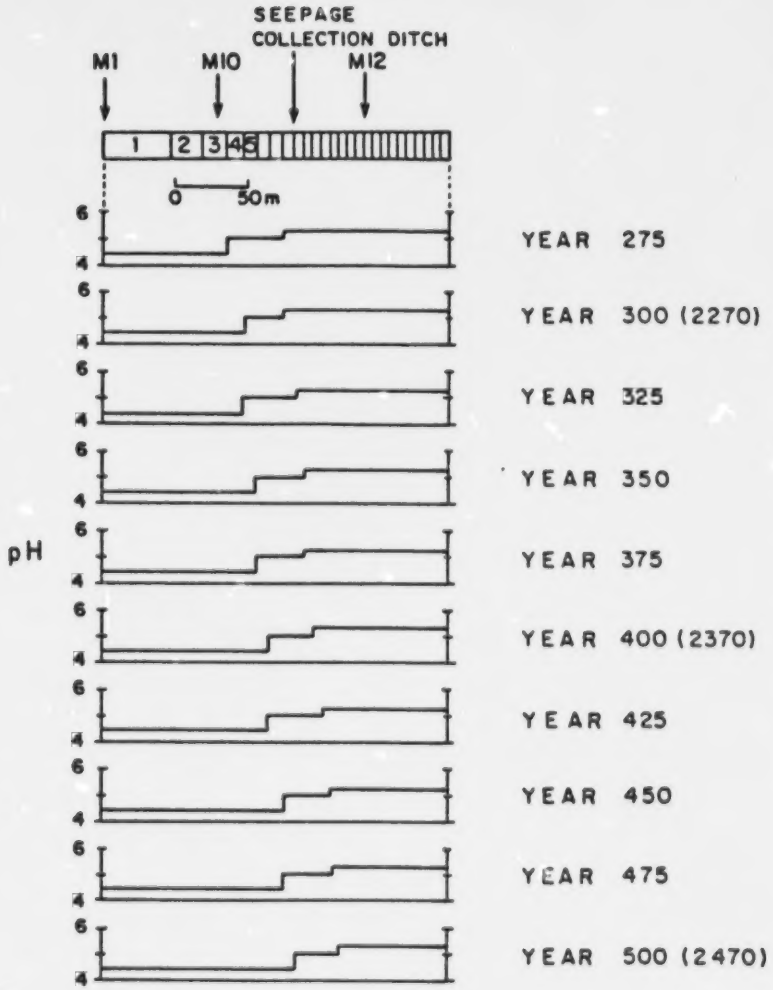

Figure 13 (continued)

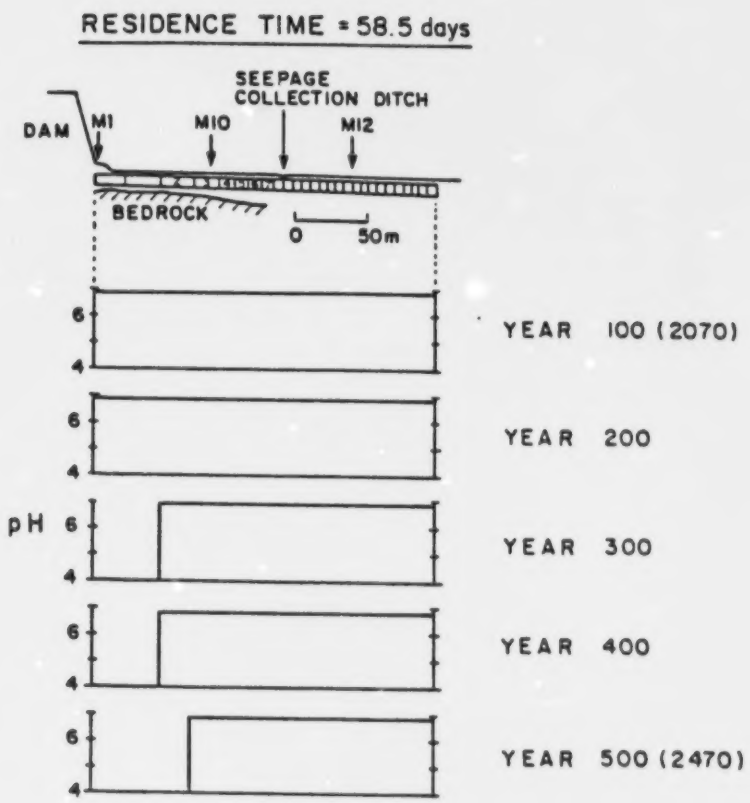

Figure 14. Prediction of future contaminant migration with a very dilute solution at pH 4.

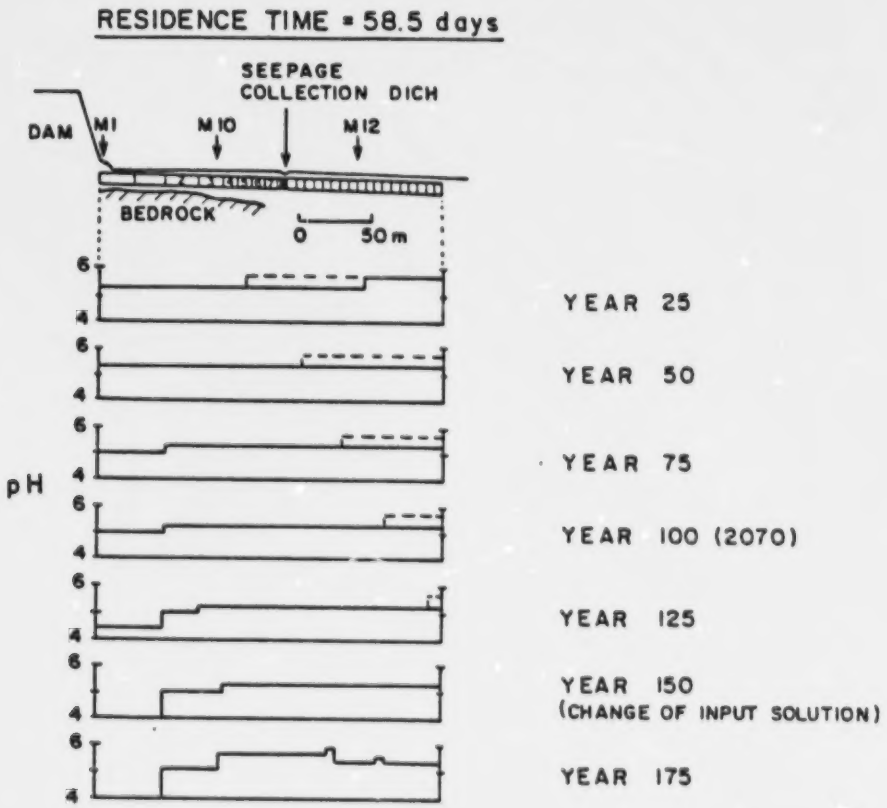

Figure ~~14~~ 15. Predictions of future contaminant migration with a dilute gypsum-saturated solution beginning at Year 150. (Dashed lines represent hand-calculated locations of the calcite sub-region)

Appendix A

ADNEUT3 INSTRUCTIONS, SAMPLE INPUT, SAMPLE OUTPUT, DEFINITION OF VARIABLES, LISTING, AND FLOWCHART

N.B. The line length of the following has been adjusted in order to fit within the format of this document.

A.1 INSTRUCTIONS FOR INPUT

** Units for input: METERS for length, DAYS for time, MOL/L for aqueous species, and WEIGHT-PERCENT for minerals **

CARD 1 (I10,2E15.6,2F10.4): N=number of cells, TINT=residence time, TIME=total time of simulation, POR=porosity, SPGR=overall specific gravity of solid matrix

CARDS 2 to [N+1] (2E15.5): CLEN=length of cell, CVEL=average linear groundwater velocity in cell

CARD [N+2] (I10,2F10.2,I10): NIN=number of input solutions; TEM=temperature in celsius; Z1, if =0, all aqueous concentrations are printed, if =1, only total concentrations are printed; IN=every IN'th time step, concentrations are printed

CARD [N+3] (4E10.3): TIMIN=time from 0.0 at which solution number NIN is used; Species 46=pH, 51=pe, 34=Total Si

CARD [N+4] (7E10.3): Species 60=Total Fe, 63=Total Ca, 64=Total Mg, 65=Total K, 59=Total Na, 58=Total Mn, 57=Total Al

CARD [N+5] (4E10.3): Species 56=Total SO4, 54=Total Cl, 53=Total F, 52=Dissolved Inorganic Carbon

** N.B. The last 3 cards are repeated for every input solution for a total of NIN times **

CARDS [N+3+(NIN*3)] to [2N+3+(NIN*3)] (5F10.5): Species 67=calcite, 68=siderite, 69=gypsum, 70=$Fe(OH)_3$, 71=$Al(OH)_3$ in weight-percent

CARDS [2N+4+(NIN*3)] to [2N+7+(NIN*3)] (5F10.5): CKA(L,NN)= solubility products for each mineral in each sub-region, where L is sub-region (1=calcite, 2=siderite, 3=$Al(OH)_3$, and 4=$Fe(OH)_3$) and NN is mineral (1=calcite, 2=siderite, 3=gypsum, 4=$Fe(OH)_3$, and 5=$Al(OH)_3$).

A.2 SAMPLE INPUT

```
         2     1.0         2.0                0.36       2.97
    1.0             1.0
    1.0             1.0
         1   10.0      0.0                 1
  0.0         4.40       3.64      4.510E-04
 9.310E-02 1.000E-02 1.646E-02 3.197E-03 6.090E-04
                                 7.099E-04 7.000E-03
 1.320E-01 4.231E-04 1.632E-03 8.000E-03
  0.85
  0.85
  -9.98      -9.34      -4.63      -37.10     -33.61
  -9.98     -10.34      -4.63      -37.10     -32.11
  -9.98     -10.34      -4.63      -37.10     -32.71
  -9.98     -10.34      -4.63      -37.10     -32.71
```

A.3 SAMPLE OUTPUT

```
 **** CELL AND TIME DATA ****
   NUMBER OF CELLS=     2  POROSITY OF AQUIFER=  0.3600
                AND SPECIFIC GRAVITY OF SOLIDS=  2.9700
   THERE WILL BE  3 TIME-STEPS OF 1.000000 DAYS EACH
   FOR A TOTAL OF  3.000E 00 DAYS (8.2191750E-03 YEARS)

   FOR CELL     1 LENGTH IS      1.00000 METERS;
     GROUNDWATER VELOCITY IS     1.00000E 00 M/DAY
     AND COVERS THE DISTANCE FROM  0.00000 METERS
                                TO 1.00000 METERS

   FOR CELL     2 LENGTH IS      1.00000 METERS;
     GROUNDWATER VELOCITY IS     1.00000E 00 M/DAY
     AND COVERS THE DISTANCE FROM  1.00000 METERS
                                TO 2.00000 METERS



 **** INPUT CHEMISTRY ****
  TEMP=  10.00 CELSIUS
```

```
 AQUEOUS CONCENTRATIONS WILL BE PRINTED
                    EVERY 1 TIME-STEPS


**** INPUT SOLUTION  1 (BEGINS AFTER   0.000000 DAYS)

*** AQUEOUS CHEMISTRY - CONCENTRATIONS IN MOL/L H2O
IONIC STRENGTH = 0.3345
PH =  4.40   PE =  3.64
H +=    5.038D-05 OH -=     9.642D-11
FE 2+= 5.771D-02 FESO4 0= 3.539D-02 FEOH += 3.476D-08
FE 3+=  9.907D-11 FESO4 +=  2.235D-10
             FEOH 2+=   6.157D-10 FE(OH)2 +=  3.201D-09
CA 2+= 5.482D-03 CASO4 0= 4.517D-03 CAHCO3 += 6.152D-07
MG 2+= 1.067D-02 MGSO4 0= 5.789D-03 MGHCO3 += 9.031D-07
K +=   2.925D-03 KSO4 -=  2.719D-04
NA +=  5.677D-04 NASO4 -= 4.133D-05
MN 2+= 6.063D-04 MNSO4 0= 1.028D-04 MNHCO3 += 5.791D-07
                 MNCL +=  2.037D-07 MN 3+=    8.426D-26
AL 3+= 3.096D-03 ALSO4 += 1.029D-03 AL(SO4)2-=1.234D-03
                  ALF 2+= 1.594D-03 AL(F)2 += 1.875D-05
ALOH 2+=2.062D-05 AL(OH)2+=7.114D-06 AL(OH)30=1.365D-06
H4SIO4 0= 4.510D-04
SO4 2-=  8.234D-02 HSO4 -= 5.097D-05
H2CO3 0= 7.905D-03 HCO3 -= 9.333D-05 CO3 2-= 3.216D-10
F -=     6.558D-07 HF 0=   3.293D-08
CL -=    4.229D-04

* TOTAL CONCENTRATIONS
FE TOT =  9.310D-02 FE2+ TOT =  9.310D-02
             FE3+ TOT  4.139D-09 SI TOT =  4.510D-04
CA TOT =  1.000D-02 MG TOT =    1.646D-02
             K TOT =   3.197D-03 NA TOT =  6.090D-04
MN TOT =  7.099D-04 AL TOT =    7.000D-03
                                  SO4 TOT = 1.320D-01
CL TOT =  4.231D-04 F TOT =     1.632D-03
          DISSOLVED INORGANIC CARBON =  8.000D-03



**** SOLID-PHASE CONCENTRATIONS IN WT-% FOR EACH CELL
 CELL NO  CALCITE SIDERITE   GYPSUM   FE(OH)3   AL(OH)3
      1   0.85000  0.00000   0.00000   0.00000   0.00000
      2   0.85000  0.00000   0.00000   0.00000   0.00000



****      LOG10(SOLUBILITY PRODUCTS)FOR MINERALS
                                   IN EACH SUB-REGION
* SUB-REGION * CACO3  FECO3  GYPSUM  FE(OH)3  AL(OH)3
```

```
 CALCITE SUB-R -9.98  -9.34   -4.63   -37.1    -33.61

 SIDERITE SUB-R -9.98 -10.34  -4.63   -37.1    -32.11

 AL(OH)3 SUB-R -9.98  -10.34  -4.63   -37.1    -32.71

 FE(OH)3 SUB-R -9.98  -10.34  -4.63   -37.1    -32.71


************************************************************
************************************************************
** TIME =      1.00000 DAYS (      0.002740 YEARS) ***
************************************************************


*****************************   CELL NUMBER      1

*** AQUEOUS CHEMISTRY - CONCENTRATIONS IN MOL/L H2O
IONIC STRENGTH = 0.2200
PH =  5.72   PE =  1.37
H +=     2.443D-06 OH -=      2.066D-09
FE 2+=   3.347D-02 FESO4 0=   1.620D-02 FEOH +=  5.073D-07
FE 3+=   2.260D-13 FESO4 +=   6.316D-13 FEOH 2+= 3.986D-11
CA 2+=   7.920D-03 CASO4 0=   5.150D-03 CAHCO3 +=4.796D-05
MG 2+=   1.149D-02 MGSO4 0=   4.919D-03 MGHCO3 +=5.247D-05
K +=     2.984D-03 KSO4 -=    2.127D-04
NA +=    5.768D-04 NASO4 -=   3.219D-05
MN 2+=   5.987D-04 MNSO4 0=   8.012D-05 MNHCO3 +=3.086D-05
                                        MN 3+=     3.273D-28
AL 3+=   2.204D-06 ALSO4 +=   9.074D-07 AL(SO4)2 -= 8.341D-07
                   ALF 2+=    2.613D-04 AL(F)2 +=   6.279D-04
                   ALOH 2+=   4.166D-07 AL(OH)2 +=  3.616D-06
H4SIO4 0= 4.510D-04
SO4 2-=    5.374D-02 HSO4 -=   1.895D-06
H2CO3 0=   1.491D-02 HCO3 -=   4.304D-03 CO3 2-=  2.604D-07
F -=       1.141D-04 HF 0=     2.342D-07
CL -=      4.229D-04

* TOTAL CONCENTRATIONS
FE TOT =   4.966D-02 FE2+ TOT =  4.966D-02
FE3+ TOT   5.255D-09 SI TOT =    4.510E-04
CA TOT =   1.312D-02 MG TOT =      1.646D-02
K TOT =    3.197D-03 NA TOT =    6.090E-04
MN TOT =   7.099D-04 AL TOT = 9.097D-04
                     SO4 TOT = 8.033D-02
CL TOT =   4.231D-04 F TOT =       1.632D-03
DISSOLVED INORGANIC CARBON = 1.942E-02

*** SOLID-PHASE CONCENTRATIONS - IN WEIGHT-PERCENT
CALCITE =    0.74624
```

```
SIDERITE =  0.09543
GYPSUM =    0.16831
FE(OH)3 =   0.00000
AL(OH)3 =   0.00900



**********************************************************
**********************************************************
** TIME =      2.00000 DAYS (      0.005479 YEARS) ***
**********************************************************



****************************   CELL NUMBER      1

*** AQUEOUS CHEMISTRY - CONCENTRATIONS IN MOL/L H2O
IONIC STRENGTH = 0.2200
PH =  5.72   PE =  1.37
H +=     2.443D-06 OH -=      2.066D-09
FE 2+=   3.347D-02 FESO4 0=   1.620D-02 FEOH +=  5.073D-07
FE 3+=   2.260D-13 FESO4 +=   6.316D-13 FEOH 2+= 3.986D-11
CA 2+=   7.920D-03 CASO4 0=   5.150D-03 CAHCO3 +=4.796D-05
MG 2+=   1.149D-02 MGSO4 0=   4.919D-03 MGHCO3 +=5.247D-05
K +=     2.984D-03 KSO4 -=    2.127D-04
NA +=    5.768D-04 NASO4 -=   3.219D-05
MN 2+=   5.987D-04 MNSO4 0=   8.012D-05 MNHCO3 +=3.086D-05
                                        MN 3+=   3.273D-28
AL 3+=   2.204D-06 ALSO4 +=  9.074D-07 AL(SO4)2-=8.341D-07
                   ALF 2+=   2.613D-04 AL(F)2 +=6.279D-04
                   ALOH 2+=  4.166D-07 AL(OH)2+=3.616D-06
H4SIO4 0= 4.510D-04
SO4 2-=    5.374D-02 HSO4 -=   1.895D-06
H2CO3 0=   1.491D-02 HCO3 -=   4.304D-03 CO3 2-= 2.604D-07
F -=       1.141D-04 HF 0=     2.342D-07
CL -=      4.229D-04

* TOTAL CONCENTRATIONS
FE TOT =   4.966D-02 FE2+ TOT =  4.966D-02
FE3+ TOT   5.255D-09 SI TOT =   4.510E-04
CA TOT =   1.312D-02 MG TOT =     1.646D-02
K TOT =    3.197D-03 NA TOT =   6.090E-04
MN TOT =   7.099D-04 AL TOT =     9.097D-04
                        SO4 TOT = 8.033D-02
CL TOT =   4.231D-04 F TOT =      1.632D-03
DISSOLVED INORGANIC CARBON =  1.942E-02

*** SOLID-PHASE CONCENTRATIONS - IN WEIGHT-PERCENT
CALCITE =   0.64248
SIDERITE =  0.19086
GYPSUM =    0.33663
FE(OH)3 =   0.00000
```

```
AL(OH)3 =    0.01799


******************************    CELL NUMBER      2

*** AQUEOUS CHEMISTRY - CONCENTRATIONS IN MOL/L H2O
IONIC STRENGTH = 0.2200
PH =  5.72   PE =  1.37
H +=     2.443D-06 OH -=      2.066D-09
FE 2+=   3.347D-02 FESO4 0=   1.620D-02 FEOH += 5.073D-07
FE 3+=   2.260D-13 FESO4 +=   6.316D-13 FEOH 2+= 3.986D-11
CA 2+=   7.920D-03 CASO4 0=   5.150D-03 CAHCO3 +=4.796D-05
MG 2+=   1.149D-02 MGSO4 0=   4.919D-03 MGHCO3 +=5.247D-05
K +=     2.984D-03 KSO4 -=    2.127D-04
NA +=    5.768D-04 NASO4 -=   3.219D-05
MN 2+=   5.987D-04 MNSO4 0=   8.012D-05 MNHCO3 +=3.086D-05
                                        MN 3+=      3.273D-28
AL 3+=   2.204D-06 ALSO4 += 9.074D-07 AL(SO4)2-=8.341D-07
                   ALF 2+= 2.613D-04 AL(F)2 +=  6.279D-04
                   ALOH 2+= 4.166D-07 AL(OH)2 +=3.616D-06
H4SIO4 0= 4.510D-04
SO4 2-=    5.374D-02 HSO4 -=   1.895D-06
H2CO3 0=   1.491D-02 HCO3 -=   4.304D-03 CO3 2-=2.604D-07
F -=       1.141D-04 HF 0=     2.342D-07
CL -=      4.229D-04

* TOTAL CONCENTRATIONS
FE TOT =   4.966D-02 FE2+ TOT =  4.966D-02
FE3+ TOT   5.255D-09 SI TOT = 4.510E-04
CA TOT =   1.312D-02 MG TOT =    1.646D-02
K TOT =    3.197D-03 NA TOT =  6.090E-04
MN TOT =   7.099D-04 AL TOT =    9.097D-04
                        SO4 TOT = 8.033D-02
CL TOT =   4.231D-04 F TOT =     1.632D-03
DISSOLVED INORGANIC CARBON =  1.942E-02

*** SOLID-PHASE CONCENTRATIONS - IN WEIGHT-PERCENT
CALCITE =    0.85000
SIDERITE =   0.00000
GYPSUM =     0.00000
FE(OH)3 =    0.00000
AL(OH)3 =    0.00000
```

A.4 DEFINITION OF VARIABLES

N.B. Not all variables are defined here: some variables have changing uses throughout the program, and some variables are self-explanatory (e.g. HSO4 = (HSO_4^-)). There are additional explanations on comments cards within ADNEUT3.

AP = activity product for a particular mineral

ASAT = absolute value of log SI of a particular compound

CK(n) = either 1) the equilibrium constant for the total association reaction for aqueous species CONC(n,J) or 2) the solubility product of mineral CONC(n,J). Values are stored initially in subprogram BLOCK DATA for reactions at 25°C and are then changed to solution temperature via the van't Hoff Equation and HC(n). See also CONC and CKA.

CKA(NSUB,NN) = input solubility products for each mineral in each sub-region; see NSUB and NN

CLEN = length of the current cell

CVEL = average linear groundwater velocity in the current cell

CONC(n,J) = concentration of the n'th species in molar:

n = 1	$FeSO_4^0$
2	$FeSO_4^+$
3	$CaSO_4^0$
4	$MgSO_4^0$
5	KSO_4^-
6	$NaSO_4^-$
7	$MnSO_4^0$
8	$AlSO_4^+$
9	$Al(SO_4)_2^-$
10	HSO_4^-
11	$CaHCO_3^+$
12	$MgHCO_3^+$
13	$MnHCO_3^+$
14	BLANK
15	BLANK
16	BLANK
17	AlF^{2+}
18	$Al(F)_2^+$
19	HF^0
20	$FeOH^{2+}$
21	$AlOH^{2+}$
22	$FeOH^+$
23	$Fe(OH)_2^+$
24	$Al(OH)_2^+$
25	$Al(OH)_3^0$

26 Fe^{2+}
27 Fe^{3+}
28 Ca^{2+}
29 Mg^{2+}
30 K^{+}
31 Na^{+}
32 Mn^{2+}
33 Al^{3+}
34 $H_4SiO_4^0$
35 BLANK
36 SO_4^{2-}
37 $H_2CO_3^0$
38 HCO_3^-
39 CO_3^{2-}
40 BLANK
41 BLANK
42 BLANK
43 F^-
44 BLANK
45 OH^-
46 H^+
47 Mn^{3+}
48 $MnCl^+$
49 Cl^-
50 Charge-balance error
51 e^-
52 Dissolved Inorganic Carbon
53 Total F
54 Total Cl
55 BLANK
56 Total SO_4
57 Total Al
58 Total Mn
59 Total Na
60 Total Fe
61 Total Fe^{2+}
62 Total Fe^{3+}
63 Total Ca
64 Total Mg
65 Total K
66 Ionic Strength
67 $CaCO_3$ s
68 $FeCO_3$ s
69 $CaSO_4.2H_2O$§s
70 $Fe(OH)_3$ s
71 $Al(OH)_3$ s
72 BLANK
73 cell's value for NSUB

FAMT = amount of siderite in a cell during one iteration

FERAMT = amount of $Fe(OH)_3$ in a cell in one iteration

G(1) = activity coefficient for neutral species

G(2) = activity coefficient for 1+ and 1- species
etc.

GAMT = amount of gypsum in a cell in one iteration

GIBAMT = amount of $Al(OH)_3$ in a cell in one iteration

HC(n) = enthalpy of reaction for either 1) the total association reaction for species CONC(n,J) or 2) the dissolution reaction for the mineral CONC(n,J)

I = time-loop counter

IN = concentrations in cells are printed every IN'th time step

J,JJ = cell and cell-loop counters

L2 = counter to check for sub-region oscillation

LX = counter for number of attempts to reach chemical equilibrium with the solid phase

M = total number of time steps in a simulation

N = total number of cells in a simulation

NA = N + 1

NAI = N + 2; for marking beginning of array storage for input solutions

NIN = number of input solutions

NN = minerals in each sub-region: 1=calcite, 2=siderite, 3=gypsum, 4=$Fe(OH)_3$, 5=$Al(OH)_3$

NSUB = designates sub-region in which current cell lies: 1=calcite, 2=siderite, 3=$Al(OH)_3$, 4=$Fe(OH)_3$

POR = porosity in decimal form

PVOL = pore volume of the cells in liters

S3, S4 = holds initial value of SUB3 and SUB4, respectively

SAT1, SAT2, SAT3, SAT4, SAT5 = log SI during one iteration for calcite, siderite, gypsum, $Fe(OH)_3$, and $Al(OH)_3$, respectively

SPGR = overall specific gravity of the solid matrix

SUB2, SUB3, SUB4 = sub-totals for certain species for sulfate, ferrous iron, and aluminum, respectively, for use in subroutine PHSOLV

TAL1 = x-coordinate (distance from zero) of the beginning of the current cell

TAL2 = x-coordinate (distance from zero) of the end of the current cell

TAMT = amount of calcite in a cell during one iteration

TEM = temperature in degrees Celsius

TEMP = temperature in Kelvin

TIME = total time of a simulation in days

TIMIN(n) = time from 0.0 at which input solution n is used

TINT = length of time of one time step in days (= residence time of cells)

VOL = total volume of a cell in m^3

WTPV = WTSOL/PVOL

WTSOL = total weight of solids in a cell in grams

XT1 = increment variable in subroutines SPEC and PHSOLV

XXX = decrement of concentration during precipitation-dissolution

XXY = increment of concetration during precipitation-dissolution

Z1 = print flag; =0, all species concentrations are printed; =1, only total concentrations are printed

Z2, Z3, etc. = various flags throughout the main program and subroutines

A.5 ADNEUT3 LISTING

```
JOB WATFIV
      DOUBLE PRECISION CONC,XS,SUB2,H,OH,
     *CT,H2CO3,HCO3,CO3,SO4,HSO4
      DOUBLE PRECISION CA2,ALSO42,FE2,FE3,
     *AL3,SA,FA,XFE2,XSO4,XCA2
      DOUBLE PRECISION FESO4,FEOH,FEOH2,ALSO4,
     *ALOH,ALOH2,ALOH3,SUB3,SUB4
      DOUBLE PRECISION SPCAL,SPSID,SPGYP,AMT,
     *TAMT,GAMT,FAMT,FFF,TDEL,GIBAMT,S3,S4
      DOUBLE PRECISION FERAMT,XFE3,SPFER,SPGIB
C COMMON CONC(73,NN): NN --> NUMBER OF CELLS+NUMBER OF
C                            INPUT SOLUTIONS+1
      COMMON /AREA/CONC(73,30),CK(73),G(4),J
      DIMENSION HC(73),TIMIN(15),CKA(4,5)
      DATA HC/3230.,3910.,1470.,4600.,2250.,
     *1120.,3700.,2150.,2840.,4910
     *.,5410.,10370.,0.,0.,0.,00.,0.,20000.,
     *3460.,10400.,14775.,132
     *00.,0.,13345.,0.,-10000.,-15760.,0.,
     *0.0,0.0,0.0,25760.,0.0,0.0,0.0
     *,0.0,0.0,-2247.,+3617.,0.,0.,0.,
     *0.0,0.0,0.0,0.0,0.
     *0,0.0,4.9,5.0,13345.,5.2,5.3,5.4,5.5,
     *5.6,5.7,5.8,5.9,6.0,6.
     *1,6.2,6.3,6.4,6.5,6.6,-3190.,-5328.,
     *261.,0.0,12990.,7.2,7.3/                                C
*************************************************************
 *************************************************************

 ADNEUT3 (ACID-DRAINAGE NEUTRALIZATION)

 A MIXING-CELL MODEL
 ACCOMODATING LARGE PH CHANGES AND SIGNIFICANT AMOUNTS
 OF SOLID-PHASE PRECIPITATION AND DISSOLUTION
 (THIS VERSION DOES NOT IN LUDE RADIONUCLIDE
 SORPTION & SPECIATION LIKE ADNEUT2 AND DOES
 INCLUDE VARIABLE INPUT CAPABILITIES UNLIKE ADNEUT1)

 BY KEVIN MORIN
 DEPARTMENT OF EARTH SCIENCES,UNIVERSITY OF WATERLOO,
            WATERLOO,ONTARIO

 MARCH,1984.  LATEST UPDATE 4/84

 COSTS FOR DEVELOPMENT AND TESTING OF THIS MODEL WERE
 PAID FROM RESEARCH GRANTS AND RESEARCH CONTRACTS
 TO DR. JOHN CHERRY,EARTH SCIENCES,U OF WATERLOO,ONT.
 *************************************************************
 *************************************************************


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```
INPUT:

*ALL LENGTH DIMENSIONS IN METERS
*TIME IN DAYS
*POROSITY IN DECIMAL FORM

N=NO OF CELLS; TINT=RESIDENCE TIME OF GROUNDWATER IN
  EACH CELL (ALL CELLS MUST HAVE IDENTICAL RESIDENCE
  TIMES: SEE CELL BELOW); TIME=TOTAL TIME OF SIMUL-
  ATION; POR=POROSITY; SPGR=SPECIFIC GRAVITY OF SOLIDS
*****************************************************************
    READ (5,2) N,TINT,TIME,POR,SPGR
  2 FORMAT (I10,2E15.6,2F10.4)
    M=INT(TIME/TINT)
    M=M+1
    TIME=FLOAT(M)*TINT
    YE=TIME/365.
    PVOL=POR*1000.
    WTSOL=(100.**3)*SPGR*(1.-POR)
    WTPV=WTSOL/PVOL
    WRITE (6,33)
 33 FORMAT ('1**** CELL AND TIME DATA ****')
    WRITE (6,34) N,POR,SPGR,M,TINT,TIME,YE
 34 FORMAT ('   NUMBER OF CELLS=',I5,'  POROSITY OF
   *AQUIFER=',F8.4,'  AND SPECIFI  GRAVITY OF
   *SOLIDS=',F8.4/'   THERE
   *' TIME-STEPS OF',F16.6,' DAYS EACH'/
   *'   FOR A TOTAL OF',1PE22.6,
   *' DAYS (',E17.7,' YEARS)')

*****************************************************************
INPUT:

* CELL SIZES (TO ACCOUNT FOR VARIABLE VELOCITY
    THROUGH THE STREAMTUBE)

VARIABLE VELOCITY IS ACCOUNTED FOR BY VARYING THE
  LENGTH OF THE CELLS IN THE DIRECTION OF GROUNDWATER
  MOVEMENT(THE OTHER DIMENSIONS ARE IMPLICITLY ADJUSTED
  SO THAT ALL CELLS ARE OF EQUAL VOLUME); BECAUSE RES-
  IDENCE TIMES(LENGTH OF A CELL/GROUNDWATER VELOCITY IN
  THE CELL) ARE IDENTICAL, THE LONGER THE CELL, THE
  FASTER THE GROUNDWATER IS MOVING THROUGH THE CELL.
  ASSUMING THE VELOCITY FIELD OF THE SIMULATED AREA IS
  KNOWN, IT IS SUGGESTED THAT FIRST THE USER DEFINE
  THE LENGTH OF ONE CELL, THEN CALCULATE THE VALUE
  OF T=(LENGTH OF THE CELL/VELOCITY IN THE CELL),
  FINALLY CALCULATE THE LENGTH OF ALL REMAINING CELLS
  FROM (LENGTH OF CELL=T*VELOCITY IN THE CELL).

FOR INPUT, CLEN=LENGTH OF EACH CELL (N TOTAL);
  CVEL= GROUNDWATER VELOCITY IN EACH CELL
*****************************************************************
    L=1
```

```
      READ (5,3) CLEN, CVEL
    3 FORMAT (2E15.5)
      TAL1=0.0
      TAL2=CLEN
      T=CLEN/CVEL
      XT=ABS((T-TINT)/TINT)
      IF (XT.LT.0.01) GO TO 57
      WRITE (6,58) T,TINT
   58 FORMAT (//' ** ERROR **: CALCULATED RESIDENCE
     *TIME FOR CELL 1 IS',
     *E15.5,/'     WHILE INPUT RESIDENCE TIME FOR
     *ALL CELLS IS',E15.5)
      STOP
   57 WRITE (6,53) L,CLEN,CVEL,TAL1,TAL2
   53 FORMAT (/'    FOR CELL',I5,' LENGTH IS',F12.5,
     *' METERS; GROUNDWATER
     * VELOCITY IS',1PE15.5,' M/DAY'/'     AND
     *COVERS THE DISTANCE FROM'
     *,0PF14.5,' METERS TO',F14.5,' METERS')
      IF (N.LT.2) GO TO 59
      DO 52 L=2,N
      READ (5,3) CLEN,CVEL
      TT=CLEN/CVEL
      XT=ABS((TT-T)/T)
      IF (XT.LT.0.01) GO TO 54
      WRITE (6,55) T,L,TT
   55 FORMAT (//' ** ERROR **: THE RESIDENCE TIME
     *FOR THE FIRST CELL IS'
     *,E15.5,' DAYS, BUT FOR CELL',I5,' IT IS',E15.5)
      STOP
   54 TAL1=TAL2
      TAL2=TAL2+CLEN
      WRITE (6,53) L,CLEN,CVEL,TAL1,TAL2
   52 CONTINUE
   59 DO 65 L=1,15
      TIMIN(L)=1.0E+60
   65 CONTINUE

*****************************************************************
INPUT:

* SPECIES CONCENTRATIONS MUST BE MOLES/LITER
* A VALUE > 0.0 MUST BE ENTERED FOR ALL SPECIES
* (IF 0, ENTER 1.0E-08)

NIN=NO OF INPUT SOLUTIONS (IF NIN=1, ONLY ONE INPUT
  SOLUTON IS USED
  FOR THE ENTIRE SIMULATION); TEM=TEMPERATURE IN
  CELSIUS; Z1 (IF Z1=0.0, ALL AQUEOUS-
  SPECIES CONCENTRATIONS ARE PRINTED; IF Z1=1.0,
  ONLY TOTAL CONCENTRATIONS ARE PRINTED); IN=EVERY
  IN'TH TIME-STEP, CONCENTRATIONS ARE PRINTED
  (IF IN=1, THERE IS A PRINT EVERY TIME-STEP)
```

```
 TIMIN=TIME FROM 0.0 AT WHICH THE NEW INPUT SOLUTION
   IS USED (TIMIN=0. FOR THE FIRST SOLUTION);
   SPECIES 46=PH; 51=PE; 34=H4SIO4;
   60=FE TOT; 63=CA TOT; 64=MG TOT; 65=K TOT;
   59=NA TOT; 58=MN TOT; 57=AL TOT;
   56=SO4 TOT; 54=CL TOT; 53=F TOT;
   52= DISSOLVED INORGANIC CARBON.
 ************************************************************
      WRITE (6,29)
  29  FORMAT (////' **** INPUT CHEMISTRY ****')
      READ (5,2252) NIN,TEM,Z1,IN
 2252 FORMAT (I10,2F10.2,I10)
 VAN'T HOFF
      TEMP=TEM+273.15
      DO 2210 KZ6=1,73
      RZ=(2.3026*(CK(KZ6))-0.5032054*HC(KZ6)/TEMP
     **+0.0016878*HC(KZ6))
      CK(KZ6)=EXP(RZ)
 2210 CONTINUE
      CK(50)=CK(38)*CK(39)

      WRITE (6,2253) TEM,IN
 2253 FORMAT ('  TEMP=',F7.2,' CELSIUS'/'  AQUEOUS
     *CONCENTRATIONS WILL BE
     *PRINTED EVERY',I7,' TIME-STEPS')
      A=1.825E+06*(78.30*TEMP)**(-1.5)
      NAI=N+2
      DO 11 L=1,NIN
      NIT=N+1+L
      DO 2261 K=1,73
      CONC(K,NIT)=0.0
 2261 CONTINUE
      READ (5,2250) TIMIN(L),CONC(46,NIT),CONC(51,NIT),
     *CONC(34,NIT)
 2250 FORMAT (4E10.3)
      READ (5,2251) CONC(60,NIT),CONC(63,NIT),
     *CONC(64,NIT),CONC(65,NIT),
     *CONC(59,NIT),CONC(58,NIT),CONC(57,NIT)
 2251 FORMAT (7E10.3)
      READ (5,2250) CONC(56,NIT),CONC(54,NIT),
     *CONC(53,NIT),CONC(52,NIT)
      CONC(46,NIT)=10.**(-CONC(46,NIT))
      CONC(51,NIT)=10.**(-CONC(51,NIT))
  SPECIATE INPUT
      CONC(27,NIT)=CONC(60,NIT)/(CK(26)*CONC(51,NIT)+1.0)
      CONC(26,NIT)=CONC(60,NIT)-CONC(27,NIT)
      CONC(61,NIT)=CONC(26,NIT)
      CONC(62,NIT)=CONC(27,NIT)
      CONC(28,NIT)=CONC(63,NIT)
      CONC(29,NIT)=CONC(64,NIT)
      CONC(30,NIT)=CONC(65,NIT)
      CONC(31,NIT)=CONC(59,NIT)
      CONC(32,NIT)=CONC(58,NIT)
      CONC(33,NIT)=CONC(57,NIT)
```

```
      CONC(36,NIT)=CONC(56,NIT)
      CONC(37,NIT)=CONC(52,NIT)
      CONC(38,NIT)=CONC(52,NIT)
      CONC(43,NIT)=CONC(53,NIT)
      CONC(49,NIT)=CONC(54,NIT)
      J=NIT
      Z2=0.0
      Z4=2.0
      CALL SPEC (A,Z2,Z4)
      WRITE (6,30) L,TIMIN(L)
   30 FORMAT(//' **** INPUT SOLUTION',I3,' (BEGINS
     *AFTER',F17.6,' DAYS)')
      Z3=1.0
      CALL PRINT (Z1,Z3,WTPV)
   11 CONTINUE

      WRITE (6,9)
    9 FORMAT(/////' **** SOLID-PHASE CONCENTRATIONS IN
     *WT-% FOR EACH CELL'/'  CELL NO.  CALCITE
     *  SIDERITE    GYPSUM   FE(OH)3   AL(OH)3')

*************************** ******************************
INPUT:

* SOLID-PHASE CONCENTRATIONS IN WEIGHT-PERCENT
       FOR EACH CELL

SPECIES 67=CALCITE; 68=SIDERITE; 69=GYPSUM; 70=FE(OH)3;
        71=AL(OH)3
*********** ***************************************************
      DO 7 L=1,N
      READ (5,4) CONC(67,L),CONC(68,L),CONC(69,L),
     *CONC(70,L),CONC(71,L)
    4 FORMAT (5F10.5)
      WRITE (6,8) L,CONC(67,L),CONC(68,L),CONC(69,L),
     *CONC(70,L),CONC(71,L)
    8 FORMAT (I10,5F10.5)
      CONC(73,L)=1.0
      CONC(70,L)=CONC(70,L)*WTPV/(100.*106.9)
      IF (CONC(70,L).GT.0.0) CONC(73,L)=4.0
      CONC(71,L)=CONC(71,L)*WTPV/(100.*78.)
      IF (CONC(71,L).GT.0.0) CONC(73,L)=3.0
      CONC(68,L)=CONC(68,L)*WTPV/(100.*116.)
      IF (CONC(68,L).GT.0.0) CONC(73,L)=2.0
      CONC(67,L)=CONC(67,L)*WTPV/(100.*100.)
      IF (CONC(67,L).GT.0.0) CONC(73,L)=1.0
      CONC(69,L)=CONC(69,L)*WTPV/(100.*172.)
    7 CONTINUE
      FFF=1.0E-06*WTPV/(100.*100.)

************************************************************
INPUT:

* INPUT OF EQUILIBRIUM CONSTANTS (SOLUBILITY PRODUCTS)
```

```
      FOR MINERALS IN EACH SUB-REGION
      AS LOG10(SP) AT SOLUTION TEMPERATURE

*  INPUT OCCURS IN THE ORDER: CALCITE SUB-REGION,
      SIDERITE SUB-R, AL(OH)3 SUB-R, FE(OH)3 SUB-R.
      MORIN (1983) FOUND THAT GYPSUM OFTEN
      DOES NOT FORM AN INDEPENDENT SUB-REGION AND
      ONE VALUE FOR GYPSUM
      SOLUBILITY CAN OFTEN BE USED FOR ALL SUB-REGIONS.

 INPUT CKA(L,NN) WHERE L DENOTES THE SUB-REGION
   (1=CALCITE,2=SIDERITE, 3=AL(OH)3, 4=FE(OH)3)
   AND NN DENOTES MINERALS (1=CACO3, 2=FECO3,
   3=CASO4.2H2O, 4=FE(OH)3, 5=AL(OH)3).
   IF THE STANDARD (INTERNAL)
   SOLUBILITY FOR THE MINERAL IS DESIRED, INPUT 0.0
 ************************************************************
      DO 5 L=1,4
      READ (5,6) CKA(L,1),CKA(L,2),CKA(L,3),
     *CKA(L,4),CKA(L,5)
    6 FORMAT (5F10.4)
      DO 61 L2=1,5
      L3=66+L2
      IF (CKA(L,L2).EQ.0.0) CKA(L,L2)=ALOG10(CK(L3))
   61 CONTINUE
    5 CONTINUE
      WRITE (6,62)
   62  FORMAT(/////' ****      LOG10(SOLUBILITY PRODUCTS)
     *FOR MINERALS IN EACH SUB-REGION'
     */' * SUB-REGION *      CACO3     FECO3 CASO4.2H2O
     *FE(OH)3    AL(OH)3'/)
      WRITE (6,63) (CKA(L,1),CKA(L,2),CKA(L,3),
     *CKA(L,4),CKA(L,5),L=1,4)
   63 FORMAT ('  CALCITE SUB-R',1F10.4,4F10.4//'
     *SIDERITE SUB-R',5F10.4//'  AL(OH)3 SUB-R
     *',5F10.4//'  FE(OH)3 SUB-R',5F10.4)
      DO 72 L=1,4
      DO 73 L2=1,5
      CKA(L,L2)=10.**(CKA(L,L2))
   73 CONTINUE
   72 CONTINUE
  MISCELLANEOUS DATA
      NA=N+1
      SQ=SQRT(CK(67))
      SR=SQRT(CK(68))
      SS=SQRT(CK(69))
      ST=SQRT(SQRT(CK(70)))
      SU=SQRT(SQRT(CK(71)))
      ITIME=2
      II=0
      NN=1


  *** TIME LOOP ***
```

```
      DO 110 I=1,M
      Z21=0.0
      Z3=0.0
      TTT=I*TINT
      IF (TTT.LT.TIMIN(ITIME)) GO TO 127
      YE=TTT/365.
      WRITE (6,2256) ITIME,TTT,YE
 2256 FORMAT ('1 '/////' ***** INPUT SOLUTION',I5,
     *' BEGINS AT TIME=',
     *F14.5,' DAYS (',F15.6,' YEARS)')
      ITIME=ITIME+1
      NAI=NAI+1
  127 II=II+1
      IF (I.EQ.M) II=IN
      IF (II.LT.IN) GO TO 126
      Z21=1.0
      II=0
      TTT=I*TINT
      YE=TTT/365.
      WRITE (6,41)
   41 FORMAT ('1*****************************************',
     X/' ************************************************')
      WRITE (6,35) TTT,YE
   35 FORMAT (' * TIME =',F13.5,' DAYS (',F14.6,' YEARS)'
     */' *****************************************'/)
  126 DO 150 MO=1,66
      CONC(MO,1)=CONC(MO,NAI)
  150 CONTINUE

 **** CELL LOOP ****
  116 DO 111 JJ=1,NN
      J=JJ
      IF (J.LT.NA) GO TO 42
      IF (Z21.EQ.0.0) GO TO 163
      WRITE (6,43)
   43 FORMAT (//' ************************   EFFLUENT')
      Z3=1.0
      GO TO 163
   42 IF (Z21.EQ.0.0) GO TO 47
      WRITE (6,36) J
   36 FORMAT (///' **************   CELL NUMBER ',I5)

   47 TAMT=CONC(67,J)
      FAMT=CONC(68,J)
      GAMT=CONC(69,J)
      FERAMT=CONC(70,J)
      GIBAMT=CONC(71,J)
  SET-UP FOR REACTIONS
      CA2=CONC(28,J)
      FE2=CONC(26,J)
      FE3=CONC(27,J)
      FESO4=CONC(2,J)
      FEOH=CONC(20,J)
      FEOH2=CONC(23,J)
```

```
      H=CONC(46,J)
      OH=CONC(45,J)
      SO4=CONC(36,J)
      HSO4=CONC(10,J)
      AL3=CONC(33,J)
      ALSO4=CONC(8,J)
      ALSO42=CONC(9,J)
      ALOH=CONC(21,J)
      ALOH2=CONC(24,J)
      ALOH3=CONC(25,J)
      SUB3=CONC(62,J)
      S3=SUB3
      SUB4=CONC(33,J)+CONC(8,J)+CONC(21,J)+CONC(24,J)+
     *CONC(25,J)+CONC(9, J)
      S4=SUB4
      CT=CONC(37,J)+CONC(38,J)+CONC(39,J)
      H2CO3=CONC(37,J)
      HCO3=CONC(38,J)
      CO3=CONC(39,J)
      SUB2=CONC(36,J)+CONC(10,J)
      XS=CONC(38,J)+2.0*CONC(39,J)-2.0*CONC(26,J)
     *-3.0*CONC(27,J)-2.0*CON
     *C(28,J)-3.0*CONC(33,J)+CONC(10,J)+2.0*CONC(36,J)
     *-CONC(46,J)+CONC(4
     *5,J)-CONC(2,J)-2.0*CONC(20,J)-CONC(23,J)-
     *CONC(8,J)-2.0*CONC(21,J)-
     *CONC(24,J)+CONC(9,J)
      SII=DSQRT(CONC(66,J))
      GAM=(-A)*SII/(1.0+SII)
      G(1)=10.**(-0.5*CONC(66,J))
      DO 2301 IS=2,4
      G(IS)=10.**((IS-1)**2.0*GAM+0.3*CONC(66,J))
2301  CONTINUE
      LX=0
      NSUB=IDINT(CONC(73,J))
      L2=0
      FFTT=0.8
      IF (CONC(57,J).LT.2.0E-03) FFTT=0.2
C CALCITE
304   Z5=0.0
      Z4=0.0
      LX=LX+1
      IF (LX.LT.250) GO TO 317
      WRITE (6,318)
 318  FORMAT (//' * SOLID-PHASE EQUILIBRIUM NOT ATTAINED
     *AFTER 250 ATTEMPTS, EXECUTION HALTED *')
      STOP
317   IYY=0
313   AP=CA2*G(3)*CO3*G(3)
      SAT1=ALOG10(AP/CKA(NSUB,1))
      ASAT=ABS(SAT1)
      IF (ASAT.LT.0.05) GO TO 308
      IYY=IYY+1
      IF (IYY.LT.2) ASATT=ASAT
```

```
      SPCAL=CA2
      IF (CT.LT.CA2) SPCAL=CT
      IF (SAT1.LT.0.0) GO TO 306
      XXX=0.020
      IF (SAT1.GT.1.2) XXX=0.3
      AMT=(XXX*SPCAL*(-1.0))
      GO TO 309
306   XXY=0.030
      IF (TAMT.LT.FFF) GO TO 307
      IF (SAT1.LT.-1.5) XXY=0.5
      STD=0.0
      IF (SAT1.LT.-8.0) STD=SQ
      AMT=STD+(SPCAL*XXY)
      IF(AMT.LT.TAMT) GO TO 309
      AMT=TAMT
309   TAMT=(-AMT+TAMT)
310   CA2=AMT+CA2
      CT=AMT+CT
      Z5=1.0
      DELSAT=ABS(ASAT-ASATT)
      IF (DELSAT.GT.2.5) GO TO 27
 302  CALL PHSOLV(XS,SUB2,H,OH,CT,H2CO3,HCO3,CO3,SO4,
     *HSO4,CA2,FE2,FE3,AL
     *3,ALSO4,ALSO42,ALOH,ALOH2,ALOH3,FESO4,
     *FEOH,FEOH2,SUB3,SUB4)
      GO TO 313
 307  TAMT=0.0
308   CONTINUE
C SIDERITE
401   IYY=0
      Z4=1.0
      IF (TAMT.LE.FFF*10.) IYY=2
 421  IXX=2+IYY
      XCA2=CA2
412   AP=FE2*G(3)*CO3*G(3)
      SAT2=ALOG10(AP/CKA(NSUB,2))
      ASAT=ABS(SAT2)
      IF (ASAT.LT.0.05) GO TO 407
      IYY=IYY+1
      IF (IYY.LT.IXX) ASATT=ASAT
      IF (IYY.GT.2) GO TO 418
      IF (ASAT.LT.0.5) GO TO 418
      XFE2=XCA2*CKA(NSUB,2)/CKA(NSUB,1)
      FA=FE2-XFE2
      IF (SAT2.LT.0.0) GO TO 418
      IF (FA.LE.0.0) GO TO 418
      AMT=TAMT-FA
      IF (AMT.LE.FFF) FA=TAMT*0.5
      AMT=FA*(-1.0)
      TAMT=TAMT+AMT
      CA2=CA2-AMT
      ASAT=50.
      GO TO 409
418   SPSID=FE2
```

```
      IF (FE2.GT.CT) SPSID=CT
      IF (SAT2.LT.0.0) GO TO 406
  419 XXX=0.007
      IF (SAT2.GT.1.0) XXX=0.12
      AMT=(XXX*SPSID*(-1.0))
      GO TO 408
  406 XXY=0.010
      IF (FAMT.LE.FFF) GO TO 416
      IF (SAT2.LT.-0.9) XXY=0.07
      STD=0.0
      IF (SAT2.LT.-6.0) STD=SR*10.
      AMT=STD+(SPSID*XXY)
      IF (AMT.LT.FAMT) GO TO 408
      AMT=FAMT
  408 CT=AMT+CT
  409 FAMT=(-AMT+FAMT)
  410 FE2=AMT+FE2
      Z5=1.0
      DELSAT=ABS(ASAT-ASATT)
      IF (DELSAT.GT.2.5) GO TO 27
      CALL PHSOLV(XS,SUB2,H,OH,CT,H2CO3,
     *HCO3,CO3,SO4,HSO4,CA2,FE2,FE3,AL
     *3,ALSO4,ALSO42,ALOH,ALOH2,ALOH3,FESO4,
     *FEOH,FEOH2,SUB3,SUB4)
      GO TO 412
  416 FAMT=0.0
  407 CONTINUE
C FE(OH)3
  692 Z4=3.0
      IYY=0
  601 AP=FE3*G(4)*(OH*G(2))**3
      SAT4=ALOG10(AP/CKA(NSUB,4))
      ASAT=ABS(SAT4)
      IF (ASAT.LT.0.05) GO TO 608
      IYY=IYY+1
      IF (IYY.LT.2) ASATT=ASAT
      SPFER=SUB3
      IF (SAT4.LT.0.0) GO TO 606
      XXX=0.04
      IF (SAT4.GT.1.3) XXX=0.1
      AMT=(XXX*SPFER*(-1.0))
      GO TO 609
  606 XXY=0.06
      IF (FERAMT.LT.FFF*1.0E-03) GO TO 607
      IF (SAT4.LT.-2.0) XXY=0.15
      STD=0.0
      IF (SAT4.LT.-8.0) STD=ST
      AMT=STD+(SPFER*XXY)
      IF (AMT.LT.FERAMT) GO TO 609
      AMT=FERAMT
  609 FERAMT=FERAMT-AMT
      XFE3=SUB3
      SUB3=AMT+SUB3
      Z5=1.0
```

```
      IF (SUB3.LT.1.0E-20.AND.XFE3.LT.1.0E-20)GO TO 601
      DELSAT=ABS(ASAT-ASATT)
      IF (DELSAT.GT.2.5) GO TO 27
      CALL PHSOLV(XS,SUB2,H,OH,CT,H2CO3,
     *HCO3,CO3,SO4,HSO4,CA2,FE2,FE3,AL
     *3,ALSO4,ALSO42,ALOH,ALOH2,ALOH3,FESO4,
     *FEOH,FEOH2,SUB3,SUB4)
      GO TO 601
  607 FERAMT=0.0
  608 CONTINUE
C AL(OH)3
  792 Z4=4.0
      IF (Z5.EQ.0.0) GO TO 714
      IF (LX.LT.12) GO TO 504
  714 IYY=0
  701 AP=AL3*G(4)*(OH*G(2))**3
      SAT5=ALOG10(AP/CKA(NSUB,5))
      ASAT=ABS(SAT5)
      IF (ASAT.LT.0.05) GO TO 708
      IYY=IYY+1
      IF (IYY.LT.2) ASATT=ASAT
      SPGIB=SUB4
      IF (SAT5.LT.0.0) GO TO 706
      XXX=0.01*FFTT
      IF (SAT5.GT.1.7) XXX=0.09*FFTT
      AMT=(XXX*SPGIB*(-1.0))
      GO TO 709
  706 XXY=0.025*FFTT
      IF (GIBAMT.LT.FFF*1.0E-02) GO TO 707
      IF (SAT5.LT.-2.0) XXY=0.05*FFTT
      STD=0.0
      IF (SAT5.LT.-8.0) STD=SU
      AMT=STD+(SPGIB*XXY)
      IF (AMT.LT.GIBAMT) GO TO 709
      AMT=GIBAMT
  709 GIBAMT=GIBAMT-AMT
      SUB4=SUB4+AMT
      Z5=1.0
      DELSAT=ABS(ASAT-ASATT)
      IF (DELSAT.GT.1.5) GO TO 27
      CALL PHSOLV(XS,SUB2,H,OH,CT,H2CO3,
     *HCO3,CO3,SO4,HSO4,CA2,FE2,FE3,AL
     *3,ALSO4,ALSO42,ALOH,ALOH2,ALOH3,FESO4,
     *FEOH,FEOH2,SUB3,SUB4)
      GO TO 701
  707 GIBAMT=0.0
  708 CONTINUE
C GYPSUM
  504 IYY=0
      IF (TAMT.LE.FFF*10.) IYY=1
      Z4=2.0
  512 AP=CA2*G(3)*SO4*G(3)
      SAT3=ALOG10(AP/CKA(NSUB,3))
      ASAT=ABS(SAT3)
```

```
      IF (ASAT.LT.0.05) GO TO 507
      IYY=IYY+1
      IF (IYY.GT.1) GO TO 502
      XSO4=CO3*CK(69)/CK(67)
      SA=SO4-XSO4
      IF (SAT3.LT.0.0) GO TO 501
      IF (SA.LE.0.0) GO TO 502
      IF (SA.GT.CA2) SA=0.9*CA2
      AMT=TAMT-SA
      IF (AMT.LE.FFF) SA=TAMT*0.5
      AMT=SA*(-1.0)
      TAMT=TAMT+AMT
      CT=CT-AMT
      GO TO 517
  501 IF (SA.GE.0.0) GO TO 502
      IF (GAMT.LE.FFF) GO TO 519
      AMT=GAMT+SA
      IF (AMT.LE.FFF) SA=GAMT*0.5
      AMT=SA*(-1.0)
      GO TO 516
  502 SPGYP=SO4
      IF (SO4.GT.CA2) SPGYP=CA2
      IF (SAT3.LT.0.0) GO TO 506
      XXX=0.06
      IF (SAT3.GT.0.25) XXX=0.5
      AMT=(XXX*SPGYP*(-1.0))
      GO TO 516
  506 XXY=0.05
      IF (GAMT.LE.FFF) GO TO 519
      IF (SAT3.LT.-0.25) XXY=0.6
      STD=0.0
      IF (SAT3.LT.-6.0) STD=SS*0.01
      AMT=STD+(SPGYP*XXY)
      IF (AMT.LT.GAMT) GO TO 516
      AMT=GAMT
  516 CA2=CA2+AMT
  517 SO4=SO4+AMT
      GAMT=GAMT-AMT
      Z5=1.0
      GO TO 512
  519 GAMT=0.0
  507 CONTINUE
C ITERATION CHECKS
      IF (Z5.EQ.0.0) GO TO 183
   27 Z2=1.0
      CONC(63,J)=CONC(63,J)-CONC(28,J)+CA2
      CONC(28,J)=CA2
      CONC(61,J)=CONC(61,J)-CONC(26,J)+FE2
      CONC(26,J)=FE2
      CONC(62,J)=CONC(62,J)-S3+SUB3
      CONC(27,J)=FE3
      CONC(60,J)=CONC(61,J)+CONC(62,J)
      CONC(56,J)=CONC(56,J)-CONC(36,J)+SO4-CONC(10,J)+HSO4
      CONC(36,J)=SO4
```

```
      CONC(10,J)=HSO4
      CONC(52,J)=CT+CONC(11,J)+CONC(12,J)+CONC(13,J)
      CONC(38,J)=HCO3
      CONC(39,J)=CO3
      CONC(57,J)=CONC(57,J)-S4+SUB4
      CONC(33,J)=AL3
      CONC(46,J)=H
      CONC(45,J)=OH
      CALL SPEC (A,Z2,Z4)
      H=CONC(46,J)
      OH=CONC(45,J)
      FE2=CONC(26,J)
      FE3=CONC(27,J)
      FESO4=CONC(2,J)
      FEOH=CONC(20,J)
      FEOH2=CONC(23,J)
      CT=CONC(37,J)+CONC(38,J)+CONC(39,J)
      H2CO3=CONC(37,J)
      HCO3=CONC(38,J)
      CO3=CONC(39,J)
      SO4=CONC(36,J)
      HSO4=CONC(10,J)
      CA2=CONC(28,J)
      AL3=CONC(33,J)
      ALSO4=CONC(8,J)
      ALSO42=CONC(9,J)
      ALOH=CONC(21,J)
      ALOH2=CONC(24,J)
      ALOH3=CONC(25,J)
      SUB3=CONC(62,J)
      S3=SUB3
      SUB4=CONC(33,J)+CONC(8,J)+CONC(21,J)+CONC(24,J)+
     *CONC(25,J)+CONC(9,J)
      S4=SUB4
      SUB2=CONC(36,J)+CONC(10,J)
      XS=CONC(38,J)+2.0*CONC(39,J)-2.0*CONC(26,J)
     *-3.0*CONC(27,J)-2.0*CON
     *C(28,J)-3.0*CONC(33,J)+CONC(10,J)+2.0*CONC(36,J)
     *-CONC(46,J)+CONC(4
     *5,J)-CONC(2,J)-2.0*CONC(20,J)-CONC(23,J)-
     *CONC(8,J)-2.0*CONC(21,J)-
     *CONC(24,J)+CONC(9,J)
      IF (Z4.EQ.1.0) GO TO 421
      IF (Z4.EQ.3.0) GO TO 692
      IF (Z4.EQ.4.0) GO TO 792
      GO TO 304
IDENTIFICATION OF IN WHICH SUB-REGION THE CELL IS AND
ADJUSTMENT OF SOLUBILITY PRODUCTS FOR THE SUB-REGION
183 L2=L2+1
      IF (L2.LT.4) GO TO 173
      WRITE (6,184) J
184 FORMAT (/' ** WARNING: POSSIBLE ERROR. CELL',I3,
     *' HAS PASSED FROM
     *ONE SUB-REGION, THROUGH 2 OTHERS,
```

```
     *AND INTO A'/'   FOURTH SUB-REGIO
     *N,    OR IS OSCILLATING BETWEEN SUB-REGIONS.
     *POSSIBLE CAUSES:'/
     *'    FAST-MOVING, SHORT SUB-REGION OR LARGE
     *VARIATION IN SOLUBILIT
     *Y OF A MINERAL BETWEEN ADJACENT'/'    SUB-REGIONS
     *CAUSING RE-ORDER
     *ING (VIA EQUILIBRIUM PHS) OF SUB-REGION OCCURRENCE.
     *EXECUTION HALTED ** '/)
      STOP
 173  IF (TAMT.EQ.0.0) GO TO 174
      IF (NSUB.EQ.1) GO TO 163
      NSUB=1
      CONC(73,J)=1.0
      GO TO 177
 174  IF (FAMT.EQ.0.0) GO TO 175
      IF (NSUB.EQ.2) GO TO 163
      NSUB=2
      CONC(73,J)=2.0
      GO TO 177
 175  IF (GIBAMT.EQ.0.0) GO TO 176
      IF (NSUB.EQ.3) GO TO 163
      NSUB=3
      CONC(73,J)=3.0
      GO TO 177
 176  IF (NSUB.EQ.4) GO TO 163
      NSUB=4
      CONC(73,J)=4.0
 177  FFTT=0.8
      IF (CONC(57,J).LT.2.0E-03) FFTT=0.2
      LX=0
      GO TO 304
C OUTPUT
 163  CONC(67,J)=TAMT
      CONC(68,J)=FAMT
      CONC(69,J)=GAMT
      CONC(70,J)=FERAMT
      CONC(71,J)=GIBAMT
      IF (Z21.EQ.0.0) GO TO 111
  40  CALL PRINT (Z1,Z3,WTPV)
111   CONTINUE
C SOLUTION TRANSPORT
 154  IF (NN.LT.NA) NN=NN+1
      DO 151 K1=2,NN
      K2=NN-K1+2
      DO 152 K3=1,66
      CONC(K3,K2)=CONC(K3,K2-1)
 152  CONTINUE
 151  CONTINUE
 110  CONTINUE
      STOP
      END
      BLOCK DATA
      DOUBLE PRECISION CONC
```

```
      COMMON /AREA/CONC(73,30),CK(73),G(4),J
      DATA CK/2.25,3.92,2.31,2.25,0.85,0.70,1.71,
     *3.02,4.92,1.99,1.00,1.0
     *7,1.72,0.0,0.0,0.00,7.01,12.75,3.17,-2.19,
     *-4.99,-9.500,-5.67,-9
     *.3,-15.0,+13.03,12.48,0.0,0.0,0.0,0.0,
     *-25.51,0.0,0.0,0.0,0.0,0.0,
     *-6.35,-10.33,0.0,0.0,0.0,0.0,-0.0,0.0,0.0,0.0,
     *0.61,4.9,5.0,-1
     *4.00,5.2,5.3,5.4,5.5,5.6,5.7,5.8,5.9,6.0,
     *6.1,6.2,6.3,6.4,6.
     *5,6.6,-8.41,-10.55,-4.62,-37.1,-31.61,7.2,7.3/
      END
      SUBROUTINE SPEC (A,[illegible],Z4)
      DIMENSION ICH(5[illegible]
      DOUBLE PRECISION [illegible]C,XS,XFE2,XSO4,SUB,Y,CC,ERR
      DOUBLE PRECISION HYD,XCA,XH,CF2,CF3,CM2,CM3,
     *XFACT,Y1,XT1,XT2
      COMMON /AREA/CONC(73,30),CK(73),G(4),J
      DATA ICH/0,1,0,0,-1,-1,0,1,-1,-
     *1,1,1,1,1,1,0,2,1,0,2,2,1,1,1,0,2,3
     *,2,2,1,1,2,3,0,0,-2,0,-1,-2,
     *0,0,0,-1,0,-1,1,3,1,-1,0/
C INITIAL VALUES
      NCT=0
2701  XT1=0.0
      NA=2
      NB=16
      ICH(50)=IDINT(CONC(44,J))
      IF (Z4.NE.2.0) NB=10
      XH=5.0E-06
      HYD=CONC(46,J)
      CONC(45,J)=CK(51)/HYD
      XFE2=CONC(26,J)
      XSO4=CONC(36,J)
      XCA=CONC(28,J)
C IONIC STRENGTH
2230  NCT=NCT+1
      IF (NCT.GT.250) RETURN
      SI=CONC(2,J)*ICH(2)**2.0+CONC(5,J)*(-ICH(5))**2.0
      DO 2300 IS=6,50,5
      SI=SI+CONC(IS,J)*IABS(ICH(IS))**2.0+CONC(
     *IS+1,J)*IABS(ICH(IS+1))**
     *2.0+CONC(IS+2,J)*IABS(ICH(IS+2))**2.0+CONC(
     *IS+3,J)*IABS(ICH(IS+3))
     ***2.0+CONC(IS+4,J)*IABS(ICH(IS+4))**2.0
2300  CONTINUE
      SI=SI*0.5 C DAVIES EQUATION
      SII=SQRT(ABS(SI))
      GAM=(-A)*SII/(1.0+SII)
      G(1)=10.**(-0.5*SI)
      DO 2301 IS=2,4
      G(IS)=10.**((IS-1)**2.0*GAM+0.3*SI)
2301  CONTINUE C H+ AND OH- COMPUTATION FOR Z2=0.0
```

```
      IF (Z2.EQ.1.0) GO TO 2236
      CONC(46,J)=HYD/G(2)
      CONC(45,J)=CK(51)/(HYD*G(2))
      CONC(47,J)=CONC(27,J)*CONC(32,J)/(CK(27)*CONC(26,J)) C
AL SPECIES
 2236 CONC(21,J)=G(4)*CK(21)/(CONC(46,J)*G(2)*G(3))
      CONC(24,J)=G(4)*CK(24)/((CONC(46,J)*G(2))**2.0*G(2))
      CONC(25,J)=G(4)*CK(25)/((CONC(46,J)*G(2))**3.0*G(1))
      CONC(17,J)=CONC(43,J)*G(4)*G(2)*CK(17)/G(3)
      CONC(18,J)=(CONC(43,J)*G(2))**2.0*G(4)*CK(18)/G(2)
 2457 CONC(8,J)=G(4)*CONC(36,J)*G(3)*CK(8)/G(2)
      CONC(9,J)=G(4)*(CONC(36,J)*G(3))**2.0*CK(9)/G(2)
 2458 Y=(CONC(21,J)+CONC(24,J)+CONC(25,J)+
     *CONC(8,J)+CONC(9,J)
     *+CONC(17,J)+CONC(18,J)+1.0)
      CONC(33,J)=CONC(57,J)/Y
      CONC(21,J)=CONC(21,J)*CONC(33,J)
      CONC(24,J)=CONC(24,J)*CONC(33,J)
      CONC(25,J)=CONC(25,J)*CONC(33,J)
      CONC(17,J)=CONC(17,J)*CONC(33,J)
      CONC(18,J)=CONC(18,J)*CONC(33,J)
      CONC(8,J)=CONC(8,J)*CONC(33,J)
      CONC(9,J)=CONC(9,J)*CONC(33,J)
C F SPECIES
 2818 CONC(19,J)=CONC(43,J)*G(2)*
     *CONC(46,J)*G(2)*CK(19)/G(1)
      CONC(17,J)=CONC(33,J)*G(4)*CONC(43,J)*G(2)*
     *CK(17)/G(3)
      CONC(18,J)=CONC(33,J)*G(4)*(
     *CONC(43,J)*G(2))**2.0*CK(18)/G(2)
      Y=(CONC(19,J)+CONC(17,J)+CONC(18,J)*2.0+CONC(43,J))
     */CONC(43,J)
      CONC(43,J)=CONC(53,J)/Y
C FE SPECIES
C   FE2+
 2465 CONC(1,J)=G(3)*G(3)*CONC(36,J)*CK(1)/G(1)
      CONC(22,J)=G(3)*CK(22)/(CONC(46,J)*G(2)*G(2))
      FACT=1.0
 2469 Y=CONC(1,J)+CONC(22,J)+1.0
      CF2=CONC(61,J)/Y
C   FE3+
 2468 CONC(2,J)=G(4)*CONC(36,J)*G(3)*CK(2)/G(2)
      CONC(20,J)=G(4)*CK(20)/(CONC(46,J)*G(2)*G(3))
      CONC(23,J)=G(4)*CK(23)/((CONC(46,J)*G(2))**2.0*G(2))
      Y1=CONC(2,J)+CONC(20,J)+CONC(23,J)+1.0
      CF3=CONC(62,J)/Y1
      IF (Z2.LT.0.5) GO TO 2411
C PE VARIABLE
      CM2=CONC(32,J)
      CM3=CONC(47,J)
      CC=CF3*CM2/(CF2*CM3)
      IF (CC.LT.0.0) GO TO 2410
      XT2=DABS((CC-CK(27))/CC)
      IF (XT2.LT.1.0E-02) GO TO 2410
```

```
      XT2=1.2
      IF (CC.LT.CK(27)) XT2=0.833
      SUB=CM3
 2404 DO 2402 I=1,300
      SUB=SUB*XT2
      HYD=SUB-CM3
      CC=(CF3-HYD)*(CM2-HYD)/((CF2+HYD)*SUB)
      IF (XT2.GT.0.99.AND.CC.LT.CK(27)) GO TO 2403
      IF (XT2.LT.1.0.AND.CC.GT.CK(27)) GO TO 2415
 2402 CONTINUE
 2403 SUB=SUB/XT2
 2415 HYD=SUB-CM3
      CM3=SUB
      CF2=CF2+HYD
      CF3=CF3-HYD
      CM2=CM2-HYD
      IF (XT2.LT.0.99) XT2=2.0
      IF (XT2.LT.1.1) GO TO 2406
      XT2=1.02
      GO TO 2404
 2406 IF (XT2.LT.1.01) GO TO 2405
      IF (Z4.LT.2.0) GO TO 2405
      XT2=1.005
      GO TO 2404
 2405 CONC(51,J)=CF2*G(3)/(CK(26)*CF3*G(4))
      CONC(32,J)=CM2
      CONC(47,J)=CM3
 2410 XFACT=Y*CF2+Y1*CF3
      XFACT=CONC(60,J)/XFACT
      CONC(26,J)=CF2*XFACT
      CONC(1,J)=CONC(1,J)*CONC(26,J)
      CONC(22,J)=CONC(22,J)*CONC(26,J)
      CONC(27,J)=CF3*XFACT
      CONC(2,J)=CONC(2,J)*CONC(27,J)
      CONC(20,J)=CONC(20,J)*CONC(27,J)
      CONC(23,J)=CONC(23,J)*CONC(27,J)
      GO TO 2412 C PE SET
 2411 Y1=Y1*G(3)/(CK(26)*CONC(51,J)*G(4))
      CONC(26,J)=CONC(60,J)/(Y+Y1)
      CONC(27,J)=CONC(26,J)*G(3)/(CK(26)*CONC(51,J)*G(4))
      CONC(1,J)=CONC(1,J)*CONC(26,J)
      CONC(22,J)=CONC(22,J)*CONC(26,J)
      CONC(2,J)=CONC(2,J)*CONC(27,J)
      CONC(20,J)=CONC(20,J)*CONC(27,J)
      CONC(23,J)=CONC(23,J)*CONC(27,J) C CA SPECIES
 2412 CONC(3,J)=G(3)*CONC(36,J)*G(3)*CK(3)/G(1)
      CONC(11,J)=G(3)*CONC(38,J)*G(2)*CK(11)/G(2)
      Y=(CONC(3,J)+CONC(11,J)+1.0)
      CONC(28,J)=CONC(63,J)/Y
      CONC(3,J)=CONC(3,J)*CONC(28,J)
      CONC(11,J)=CONC(11,J)*CONC(28,J) C MG SPECIES
      CONC(4,J)=G(3)*G(3)*CONC(36,J)*CK(4)/G(1)
      CONC(12,J)=G(3)*CONC(38,J)*G(2)*CK(12)/G(2)
      Y=(CONC(4,J)+CONC(12,J)+1.0)
```

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      CONC(29,J)=CONC(64,J)/Y
      CONC(4,J)=CONC(4,J)*CONC(29,J)
      CONC(12,J)=CONC(12,J)*CONC(29,J) C K SPECIES
      CONC(5,J)=G(2)*CONC(36,J)*G(3)*CK(5)/G(2)
      Y=CONC(5,J)+1.0
      CONC(30,J)=CONC(65,J)/Y
      CONC(5,J)=CONC(5,J)*CONC(30,J) C NA SPECIES
      CONC(6,J)=G(2)*CONC(36,J)*G(3)*CK(6)/G(2)
      Y=CONC(6,J)+1.0
      CONC(31,J)=CONC(59,J)/Y
      CONC(6,J)=CONC(6,J)*CONC(31,J) C MN SPECIES
      CONC(7,J)=G(3)*G(3)*CONC(36,J)*CK(7)/G(1)
      CONC(13,J)=G(3)*CONC(38,J)*G(2)*CK(13)/G(2)
      CONC(48,J)=G(3)*CONC(49,J)*G(2)*CK(48)/G(2)
      SUB=CONC(58,J)-CONC(47,J)
      Y=(CONC(7,J)+CONC(13,J)+CONC(48,J)+1.0)
      CONC(32,J)=SUB/Y
      CONC(7,J)=CONC(7,J)*CONC(32,J)
      CONC(13,J)=CONC(13,J)*CONC(32,J)
      CONC(48,J)=CONC(48,J)*CONC(32,J) C CL SPECIES
      CONC(49,J)=CONC(54,J)-CONC(48,J) C SO4 SPECIES
      CONC(10,J)=CONC(36,J)*G(3)*
     *CONC(46,J)*G(2)*CK(10)/G(2)
      Y=(CONC(10,J)+CONC(1,J)+CONC(2,J)+CONC(3,J)+
     *CONC(4,J)+CONC(5,J)+
     *CONC(6,J)+CONC(7,J)+CONC(8,J)+CONC(9,J)*2.0+
     *CONC(36,J))/CONC(36,J)
      CONC(36,J)=CONC(56,J)/Y C CARBONATE SPECIES
2475  CONC(38,J)=G(1)*CK(38)/(CONC(46,J)*G(2)*G(2))
      CONC(39,J)=G(1)*CK(50)/((
     *CONC(46,J)*G(2))**2.0*G(3))
      SUB=CONC(52,J)-CONC(11,J)-CONC(12,J)-CONC(13,J)
      IF (SUB.LT.0.0) SUB=CONC(52,J)*1.0E-06/(NCT+1)
      Y=CONC(38,J)+CONC(39,J)+1.0
      CONC(37,J)=SUB/Y
      CONC(38,J)=CONC(38,J)*CONC(37,J)
      CONC(39,J)=CONC(39,J)*CONC(37,J) C PH CALCULATION
      IF (Z2.LT.0.5) GO TO 4016
      NA=NA+1
      IF (NA.LT.NB) GO TO 2227
      NA=0
      XH=CONC(2,J)*ICH(2)+CONC(5,J)*ICH(5)
      DO 1303 K=6,50,5
      XH=XH+CONC(K,J)*ICH(K)+CONC(K+1,J)*ICH(K+1)+
     *CONC(K+2,J)*ICH(K+2)+C
     *ONC(K+3,J)*ICH(K+3)+CONC(K+4,J)*ICH(K+4)
1303  CONTINUE
      IF (XT1.GT.0.0) GO TO 1416
      XT1=1.2
      IF (XH.GT.0.0) XT1=0.833
      NB=6
1416  IF (XT1.GT.0.99.AND.XH.GT.0.0) GO TO 1403
      IF (XT1.LT.1.0.AND.XH.LT.0.0) GO TO 1415
      CONC(46,J)=CONC(46,J)*XT1
```

```
      CONC(45,J)=CK(51)/(CONC(46,J)*G(2)*G(2))
      GO TO 2227
1403  CONC(46,J)=CONC(46,J)/XT1
1415  CONC(45,J)=CK(51)/(CONC(46,J)*G(2)*G(2))
      IF (XT1.LT.0.99) XT1=2.0
      IF (XT1.LT.1.1) GO TO 1417
      XT1=1.02
      NB=4
      GO TO 2227
1417  IF (XT1.LT.1.01) GO TO 2226
      IF (Z4.LT.2.0) GO TO 2225
      XT1=1.005
      NB=3
      GO TO 2227
C CHARGE BALANCE CALCULATION
4016  IF (Z2.LT.0.0) GO TO 2207
      ERR=CONC(2,J)*ICH(2)+CONC(5,J)*ICH(5)
      DO 2205 K=6,50,5
      ERR=ERR+CONC(K,J)*ICH(K)+CONC(K+1,J)*ICH(K+1)+
     *CONC(K+2,J)*ICH(K+2)
     *+CONC(K+3,J)*ICH(K+3)+CONC(K+4,J)*ICH(K+4)
2205  CONTINUE
      CONC(50,J)=ICH(50)*CONC(50,J)-ERR
      ICH(50)=1
      CONC(44,J)=1.0
      IF (CONC(50,J).GT.0.0) GO TO 2207
      ICH(50)=(-1.0)
      CONC(44,J)=(-1.0)
      CONC(50,J)=DABS(CONC(50,J))
C ITERATION CHECKS
2207  NCS=0
      CHECK1=DABS((XFE2-CONC(26,J))/XFE2)
      IF (XFE2.LT.1.0E-14) CHECK1=0.0
      CHECK2=DABS((XSO4-CONC(36,J))/XSO4)
      CHECK3=DABS((XCA-CONC(28,J))/XCA)
      IF (CHECK1.LT.XH.AND.CHECK2.LT.XH) NCS=NCS+1
      IF (CHECK3.LT.XH) NCS=NCS+1
      IF (NCS.EQ.2) GO TO 2225
2226  XFE2=CONC(26,J)
      XSO4=CONC(36,J)
      XCA=CONC(28,J)
      IF (XT1.GT.0.5) GO TO 2703
2227  CONC(61,J)=CONC(26,J)+CONC(1,J)+CONC(22,J)
      CONC(62,J)=CONC(27,J)+CONC(2,J)+
     *CONC(20,J)+CONC(23,J)
      GO TO 2230
2703  HYD=CONC(46,J)*G(2)
      XH=1.0E-05
      Z2=-1.0
      XT1=0.0
      GO TO 2230
2225  CONC(61,J)=CONC(26,J)+CONC(1,J)+CONC(22,J)
      CONC(62,J)=CONC(27,J)+CONC(2,J)+
     *CONC(20,J)+CONC(23,J)
```

```
      CONC(66,J)=SI
      RETURN
      END
      SUBROUTINE PHSOLV(XS,SUB2,H,OH,CT,H2CO3,
     *HCO3,CO3,SO4,HSO4,CA2,FE2,
     *FE3,AL3,ALSO4,ALSO42,ALOH,ALOH2,ALOH3,FESO4,
     *FEOH,FEOH2,SUB3,SUB4)
      DOUBLE PRECISION CONC,XS,SUB2,XI,H,OH,CT,H2CO3,
     *HCO3,CO3,SO4,ALOH3,SUB3,SUB4
      DOUBLE PRECISION HSO4,CA2,FE2,FE3,AL3,Y,ALSO42
      DOUBLE PRECISION FESO4,FEOH,FEOH2,ALSO4,ALOH,ALOH2
      COMMON /AREA/CONC(73,30),CK(73),G(4),J
      XT1=0.0
3001  HCO3=G(1)*CK(38)/(H*G(2)*G(2))
      CO3=G(1)*CK(50)/((H*G(2))**2.0*G(3))
      Y=HCO3+CO3+1.0
      H2CO3=CT/Y
      HCO3=HCO3*H2CO3
      CO3=CO3*H2CO3
      HSO4=G(3)*H*G(2)*CK(10)/G(2)
      Y=HSO4+1.0
      SO4=SUB2/Y
      HSO4=HSO4*SO4
      FESO4=G(4)*SO4*G(3)*CK(2)/G(2)
      FEOH=G(4)*CK(20)/(H*G(2)*G(3))
      FEOH2=G(4)*CK(23)/((H*G(2))**2.0*G(2))
      Y=1.0+FESO4+FEOH+FEOH2
      FE3=SUB3/Y
      FESO4=FESO4*FE3
      FEOH=FEOH*FE3
      FEOH2=FEOH2*FE3
      ALSO4=G(4)*SO4*G(3)*CK(8)/G(2)
      ALSO42=G(4)*(SO4*G(3))**2*CK(9)/G(2)
      ALOH=G(4)*CK(21)/(H*G(2)*G(3))
      ALOH2=G(4)*CK(24)/((H*G(2))**2.0*G(2))
      ALOH3=G(4)*CK(25)/((H*G(2))**3.0*G(1))
      Y=1.0+ALSO4+ALOH+ALOH2+ALOH3+ALSO42
      AL3=SUB4/Y
      ALSO4=ALSO4*AL3
      ALSO42=ALSO42*AL3
      ALOH=ALOH*AL3
      ALOH2=ALOH2*AL3
      ALOH3=ALOH3*AL3
      XI=XS-HCO3-2.0*CO3+2.0*FE2+3.0*FE3+2.0*CA2+3.0*
     *AL3-HSO4-2.0*SO4+H-OH+
     *FESO4+2.0*FEOH+FEOH2+ALSO4+2.0*ALOH+ALOH2-ALSO42
      IF (XT1.GT.0.0) GO TO 3002
      XT1=1.33
      IF (XI.GT.0.0) XT1=0.75
3002  IF (XT1.GT.0.99.AND.XI.GT.0.0) GO TO 3003
      IF (XT1.LT.1.0.AND.XI.LT.0.0) GO TO 3004
      H=H*XT1
      OH=CK(51)/(H*G(2)*G(2))
      GO TO 3001
```

```
3003 H=H/XT1
3004 OH=CK(51)/(H*G(2)*G(2))
     IF (XT1.LT.0.99) XT1=2.0
     IF (XT1.LT.1.1) RETURN
     XT1=1.05
     GO TO 3001
     END
     SUBROUTINE PRINT (Z1,Z3,WTPV)
     DOUBLE PRECISION CONC
     COMMON /AREA/CONC(73,30),CK(73),G(4),J
     WRITE (6,3001)
3001 FORMAT(/' *** AQUEOUS CHEMISTRY -
    *CONCENTRATIONS IN MOL/L H2O')
     WRITE (6,3200) CONC(66,J)
3200 FORMAT (' IONIC STRENGTH =',F7.4)
     PH=(-DLOG10(CONC(46,J)*G(2)))
     PE=(-DLOG10(CONC(51,J)))
     WRITE (6,3000) PH,PE
3000 FORMAT (' PH =',F6.2,'   PE =',F6.2)
     IF (Z1.EQ.1.0) GO TO 3100
     WRITE (6,3201) CONC(46,J),CONC(45,J)
3201 FORMAT (' H +=',1PE13.3,' OH -=',E14.3)
     WRITE(6,3002)CONC(26,J),CONC(1,J),CONC(22,J)
3002 FORMAT(' FE 2+=',1PE11.3,' FESO4 0=',E11.3,
    *' FEOH +=',E11.3)
     WRITE (6,3003) CONC(27,J),CONC(2,J),
    *CONC(20,J),CONC(23,J)
3003 FORMAT(' FE 3+=',1PE11.3,' FESO4 +='
    *,E11.3,' FEOH 2+=',E12.3,' FE(
    *OH)2 +=',E11.3)
     WRITE (6,3004) CONC(28,J),CONC(3,J),CONC(11,J)
3004 FORMAT (' CA 2+=',1PE11.3,' CASO4 0=',E11.3,'
    *CAHCO3 +=',E11.3)
     WRITE(6,3005)CONC(29,J),CONC(4,J),CONC(12,J)
3005 FORMAT (' MG 2+=',1PE11.3,' MGSO4 0=',E11.3,'
    *MGHCO3 +=',E11.3)
     WRITE (6,3006) CONC(30,J),CONC(5,J)
3006 FORMAT (' K +=  ',1PE11.3,' KSO4 -=',E12.3)
     WRITE (6,3007) CONC(31,J),CONC(6,J)
3007 FORMAT (' NA += ',1PE11.3,' NASO4 -=',E11.3)
     WRITE(6,3008)CONC(32,J),CONC(7,J),CONC(13,J),
    *CONC(48,J),CONC(47,J)
3008 FORMAT(' MN 2+=',1PE11.3,' MNSO4 0=',E11.3,
    *' MNHCO3 +=',E12.3,' MN
    *CL +=',E13.3,' MN 3+=',E14.3)
     WRITE (6,3009) CONC(33,J),CONC(8,J),CONC(9,J),
    *CONC(17,J),CONC(18,J
    *),CONC(21,J),CONC(24,J),CONC(25,J)
3009 FORMAT(' AL 3+=',1PE11.3,' ALSO4 +=',E11.3,
    *' AL(SO4)2 -=',E10.3
    */19X,'ALF 2+=',E12.3,' AL(F)2 +=',E12.3
    */19X,'ALOH 2+=',E11.3,' AL(OH)2 +=',E11.3,
    *' AL(OH)3 0=',E10.3)
     WRITE (6,3010) CONC(34,J)
```

```
 3010 FORMAT (' H4SIO4 0=',1PE10.3)
      WRITE (6,3011) CONC(36,J),CONC(10,J)
 3011 FORMAT(' SO4 2-= ',1PE11.3,' HSO4 -=',E11.3)
      WRITE (6,3012) CONC(37,J),CONC(38,J),CONC(39,J)
 3012 FORMAT(' H2CO3 0=',1PE11.3,' HCO3 -='
     *,E11.3,' CO3 2-=',E11.3)
      WRITE (6,3014) CONC(43,J),CONC(19,J)
 3014 FORMAT (' F -=    ',1PE11.3,' HF 0=',E13.3)
      WRITE (6,3015) CONC(49,J)
 3015 FORMAT (' CL -=   ',1PE11.3)
 3100 WRITE (6,3016)
 3016 FORMAT (/' * TOTAL CONCENTRATIONS ')
      WRITE (6,3017) CONC(60,J),CONC(61,J),
     *CONC(62,J),CONC(34,J)
 3017 FORMAT (' FE TOT =',1PE11.3,' FE2+ TOT ='
     *,E11.3,' FE3+ TOT',E11.3,
     *' SI TOT =',E11.3)
      WRITE (6,3018)CONC(63,J),CONC(64,J),
     *CONC(65,J),CONC(59,J)
 3018 FORMAT (' CA TOT =',1PE11.3,' MG TOT ='
     *,E13.3,' K TOT =',E12.3,' N
     *A TOT =',E11.3)
      WRITE (6,3019) CONC(58,J),CONC(57,J),CONC(56,J)
 3019 FORMAT  (' MN TOT  =',1PE11.3,' AL TOT  =',E13.3,' SO4
TOT =',E10.3)
      WRITE (6,3020) CONC(54,J),CONC(53,J),CONC(52,J)
 3020  FORMAT('   CL  TOT  =',1PE11.3,'  F   TOT  =',E14.3,'
DISSOLVED INORGANIC
     *CARBON =',E11.3)
      IF (Z3.EQ.1.0) RETURN
      TA=CONC(67,J)*100.*100./WTPV
      FA=CONC(68,J)*100.*116./WTPV
      GA=CONC(69,J)*100.*172./WTPV
      AA=CONC(70,J)*100.*106.9/WTPV
      BA=CONC(71,J)*100.*78./WTPV
      WRITE (6,3021)
 3021 FORMAT (/' *** SOLID-PHASE CONCENTRATIONS -
     *IN WEIGHT-PERCENT')
      WRITE (6,3022) TA,FA,GA,AA,BA
 3022 FORMAT(' CALCITE =',F10.5/' SIDERITE =',
     *F9.5/' GYPSUM =',F11.
     *5/' FE(OH)3 =',F10.5/' AL(OH)3 =',F10.5)
      RETURN
      END
```

APPENDIX FIGURE

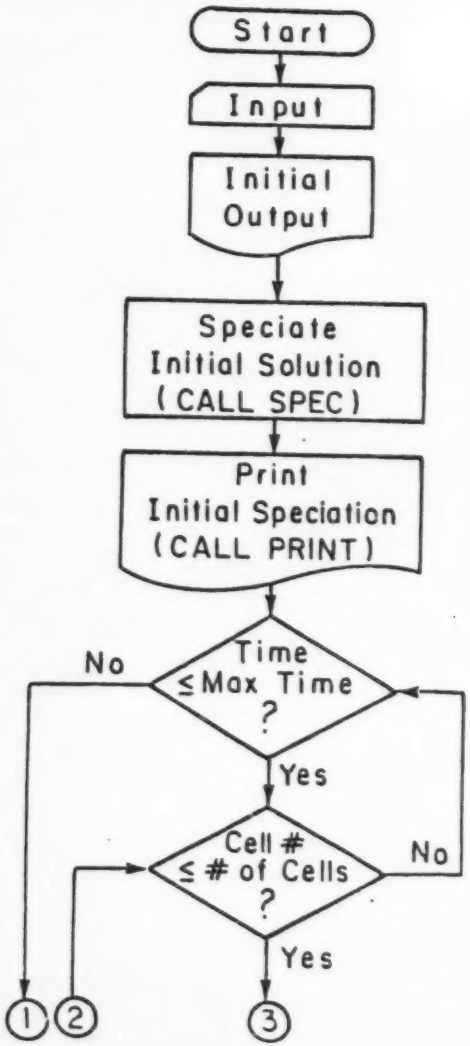

Figure A1. Flowchart for ADNEUT.

SUBROUTINES

SPEC - full speciation of all complexes

PHSOLV - speciation of only dominant complexes (used when amount of precipitation - dissolution is small)

PRINT - prints concentrations of species

PRINTN - speciates radionuclides and prints their concentration (ADNEUT2 only)

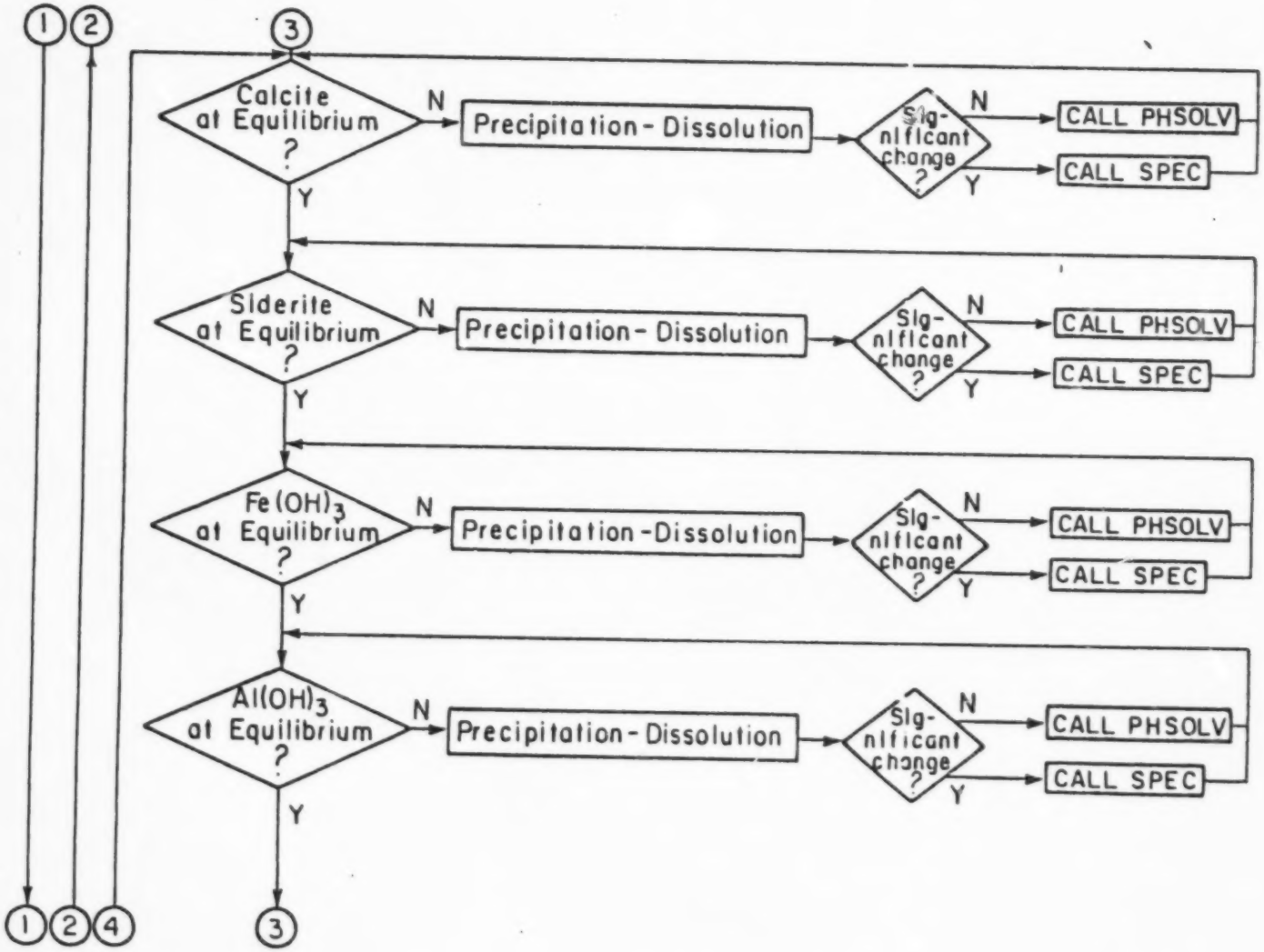

Figure A1 (continued)

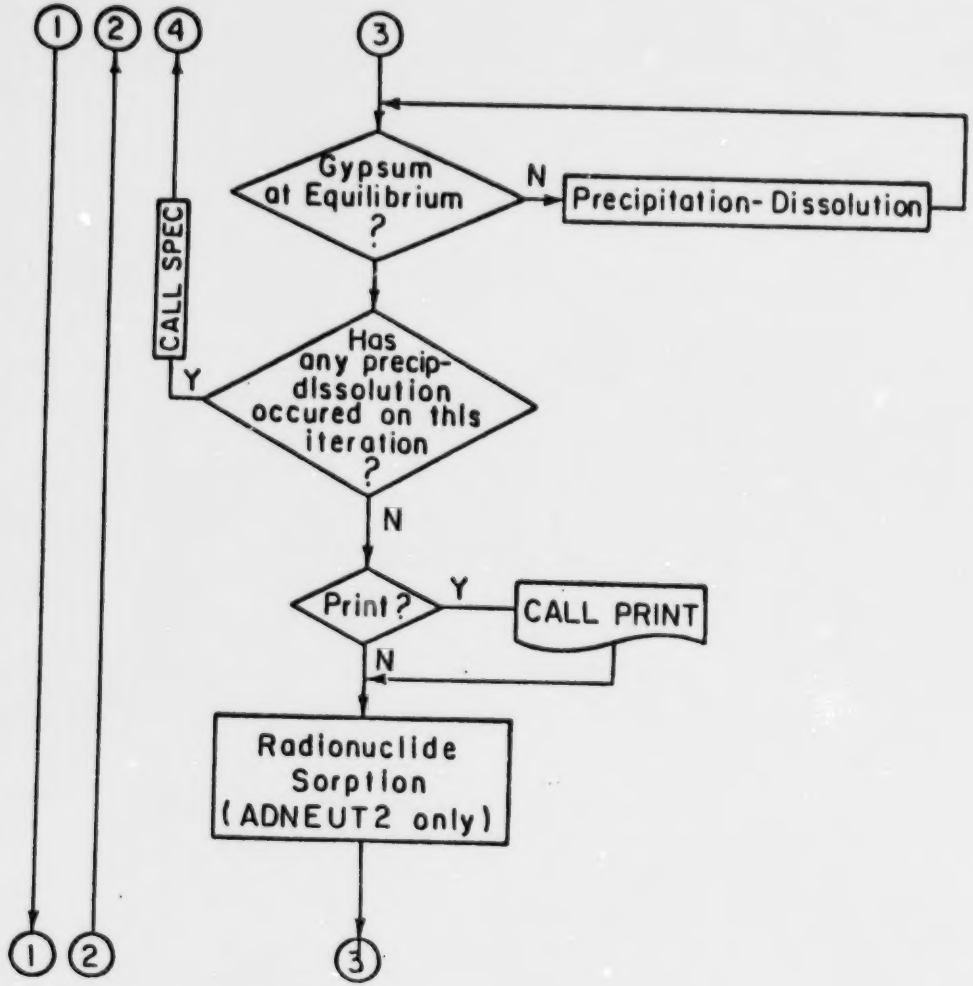

Figure A1 (continued)

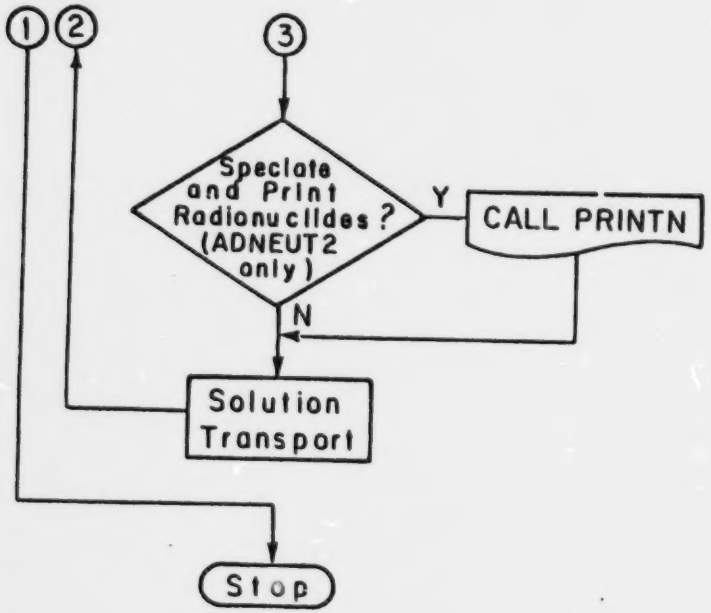

Figure A1 (continued)